# ENVIRONMENTAL ENGINEERING COLLECTION

Francis J. Hopcroft, Collection Editor



# Protecting Clean Air

Preventing Pollution

Sarah J. Simon



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SARAH J. SIMON, P.E.



Protecting Clean Air: Preventing Pollution

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### **A**BSTRACT

Having clean air to breathe is an often overlooked necessity, yet humans pollute the air through growing demand for energy and consumables. This book presents an overview of air quality, emission sources, criteria pollutants, greenhouse gases, control programs, and the impact of pollution on the atmosphere and global systems. Expertise in many fields is needed to protect air quality—politics, environmental engineering, law, planning, meteorology, health sciences, data management, and more. The book will guide readers through strategies and measures to prevent air pollution and better understand challenges that emission sources pose to society and ecosystems.

### **KEYWORDS**

acid rain, air contaminants, air monitoring, air quality, ambient air quality standard (AAQS) standard, asbestos, boiler, CAA, carbon dioxide, carbon monoxide, Clean Air Act, climate change, CO, CO<sub>2</sub>, coal, combustion, criteria pollutants, dispersion model, emission inventory, emission rate, emission source, emissions, engineering, fossil fuel, fuel, GHG, greenhouse gas, HAP, hazardous air pollutant, health effects, mercury, mobile source, NAAQS, NESHAP, New Source Review, nitrogen dioxide, nitrogen oxides, NO<sub>2</sub>, NSPS, O<sub>3</sub>, oxidation, ozone, particulate, photochemical modeling, PM, PM<sub>10</sub>, PM<sub>2.5</sub>, pollutant, preventing pollution, smog, SO<sub>2</sub>, state implementation plan (SIP), sulfur dioxide, VOC, volatile organic compounds, welfare effects

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## INTRODUCTION

Clean air to breathe is a necessity, as important as nutritious food and clean water. Humans need clean air to thrive. They also have the power to prevent air pollution. This book presents an overview of air pollution and its sources, emissions, health and welfare effects, city and government programs for controlling pollution, and tools and principles for preserving good air quality.

Contaminant releases to the air are not new; pure air would have no contaminants. Today, the earth's atmosphere contains approximately 78 percent nitrogen (N<sub>2</sub>), 21 percent oxygen (O<sub>2</sub>), 0.9 percent argon (Ar), 0.4 percent carbon dioxide (CO<sub>2</sub>), and only trace concentrations of everything else. Low concentrations of natural contamination may come from volcanos, wind, and forest fires which release significant quantities of airborne particle and gaseous contaminants. Other natural processes cause animal releases or dust particles and ocean salts to become airborne. The fragrant gases released by a pine forest, a field, or a flower garden are "contaminants" in what is called "fresh air."

Civilization has added emissions—pollutants—from many human activities. In the millennia since humans tamed fire for heat and light, people burning wood or other organic vegetation have not only signaled their presence and cooked food with fire but also made smoke. Three hundred years ago, wind and rain could clear most skies. Only a few activities by a neighbor, a wood fire or a pig farm, could intrude on the well-being and health of many other people.

By the 18th century, emissions from heating, cooking, and industry in the growing cities were contaminating the air with higher concentrations of smoke and waste odors. Coal generated more smoke and invisible gas emissions, as it met the increased demand for energy of the Industrial Revolution. By the early 1900s, liquid petroleum-burning engines offered means other than water, wind, and foot-power to transport people and goods, and they made more emissions.

Invention and engineering turned electricity into a reliable and abundant energy supply with emissions confined to the location of the generating equipment. Industrial processes and machines refined and created new materials (with emissions), including steel, textiles, building materials, plastics, and consumables. The number of vehicles on the roadways multiplied, and agricultural productivity increased, assisted by fertilizers, pesticides, and machines.

As cities and industry flourished, the choking levels of smoke drew public attention and ire, and communities started to develop air pollution control measures. The first city ordinances to prohibit or control emissions and nuisance were put in place during the 19th century. These local programs seemed to be sufficient protection for air quality until the health effects of dirty air became obvious during deadly air pollution episodes in the late 1940s and 1950s.

By the mid-20th century, a more widespread awareness of air and water pollution, nuclear fallout, and the fact that the new, miracle pesticides could cause a "silent spring" galvanized the United States into a decade of rapid advances in pollution control. As Buckminster Fuller, one of the preeminent futurists of the period, wrote:

We have been misusing, abusing and polluting this extraordinary chemical interchanging system for successfully regenerating life aboard our planetary spaceship.<sup>2</sup>

This awareness sparked a new national commitment in the United States to research and implement measures to protect the public and environment from harmful pollutant exposures and impacts. The Earth-Day movement culminated in the creation of the US Environmental Protection Agency, the Clean Air Act, and the Clean Water Act.

Local and federal air pollution control program staff have studied the causes of air pollution and found ways to set clean, yet practical, across-the-board, emission standards for equipment categories and industries. Academia, industry, and government, using a wide range of disciplines, have devised control measures and more efficient processes that reduce emission rates.

The round of air pollution control programs from the 1970s significantly reduced air pollution. They also resulted in better monitoring, only to find that initial efforts had not prevented acid rain and other

<sup>&</sup>lt;sup>1</sup>R. Carson. (1962). Silent Spring (Boston: Houghton Mifflin Company).

<sup>&</sup>lt;sup>2</sup>R. B. Fuller. (1969). *Operating Manual for Spaceship Earth* Southern (Carbondale: Illinois University Press).

undesirable long-range and global impacts, including global warming. Emission sources and air pollution levels around the globe continue to pose serious challenges to society and ecosystems.

People generate air contaminants, but engineers, scientists, and the public determine how much contamination is unacceptable and how to control emissions. The policies and strategies behind pollution control efforts push society and the economy toward more efficient, less polluting ways to achieve healthy air quality. Many benefits accrue from protecting clean air—savings from improved energy efficiency, better health, lower health care costs, more good jobs, and better quality of life. The work of preventing air pollution relies on expertise from many fields—environmental, chemical, civil, mechanical, and electrical engineering; planning and politics; meteorology and health sciences; the law; data management; and more.

This book provides a guide for understanding the factors that create air pollution and the effort that has been invested in improving and protecting air quality. By learning the basic causes of air pollution and about current progress in achieving good air quality, engineers and others can design and support solutions to protect clean air for a thriving future.

# AIR CONTAMINANTS AND THEIR SOURCES

Many physical and biological processes release contaminants into the air. Natural processes created the earth's atmosphere more than 2 billion years ago and filled it with gases and contaminants long before life evolved on the surface.

Air contaminants are emitted from geological, anthropogenic (human), and biogenic (animals, plants, and other creatures) processes and range from the natural emissions of flowers to the smoke of a coal-fired electric power plant. Despite all the particle and gas contaminants in the air, pollution is in the nose, and lungs, of the "beholder." A "contaminant" may or may not be a pollutant, depending on the effect, the atmospheric concentration, and the accepted norm.

Various contaminant sources emit particles and gaseous compounds that affect human health and welfare, but only rare releases from early human civilization could contaminate air quality more than natural processes could. The Industrial Revolution marked the beginning of the age of significant human emissions, and its legacy is air pollution. Good, or even acceptable, air quality cannot be assured until the sources, quantities, and characteristics of polluting contaminants are known.

### 2.1 NATURAL AIR CONTAMINATION SOURCES

The physical forces that have shaped earth release huge quantities of materials into the air on geological timeframes. *Particles* are released from the earth by volcanic eruptions, which in days or weeks can spew thousands of tons of ash and soil directly into the atmosphere as they

blow up mountains or tear apart the earth's crust. Volcanic ash particles are composed of rock minerals and are hard and abrasive, containing trace metals and other elements. They may provide micronutrients to the ground where the ash is deposited. Some of the ash particles from the Mount St. Helens eruption in Washington state (1980) measured less than 0.04 mm (40 microns,  $\mu \text{m}$ ).

Volcanos and earthquakes also release hot magma and chemicals in gaseous form from on-going physical and chemical changes below the earth's crust and seafloor. The gaseous chemicals include *reduced sulfur compounds* (or total reduced sulfur, TRS), including *hydrogen sulfide* (H<sub>2</sub>S), sulfuric and hydrochloric *acids* (H<sub>2</sub>SO<sub>4</sub>, HCl), *sulfur dioxide* (SO<sub>2</sub>), *carbon dioxide* (CO<sub>2</sub>), and *carbon monoxide* (CO).<sup>3</sup> Significant quantities of hot, gas emissions condense into tiny *particulate matter* (PM) as they cool in the atmosphere. Particles and dust from volcanic eruptions can take as long as a century to clear from the air, but they are finally deposited dry or absorbed into rain and snow and fall to the ground.

Over 2 billion years ago, the contaminant free oxygen ( $O_2$ ) was released as a waste by living microbes in the seas and added to the primordial atmosphere. Green plants take in  $CO_2$  and  $O_2$  for photosynthesis, a process which uses sunlight energy to combine carbon and oxygen with water ( $H_2O$ ) and store the energy in carbohydrate and other carbon-based,  $organic\ compounds$  (OC). Animal and plant ecosystems oxidize food compounds, especially carbohydrates, to release the continuous stream of energy needed to live. Most ecologies have developed remarkably balanced and elegant food chains and carbon cycles. Oxidation byproducts, including  $CO_2$  and  $H_2O$ , are cycled back into the air.

Over the past 500 million years, periodic meteor strikes have added PM and smoke emissions to the atmosphere for periods lasting hundreds of thousands of years. The major collisions have been large enough to release much more material into the atmosphere than the largest volcanic eruptions and have created fires around the globe. Research shows that the dust and smoke PM of these extraterrestrial impacts remained in the atmosphere for long periods and lowered temperatures well below the pre-collision climatic averages. Mass extinctions occurred at the time

<sup>&</sup>lt;sup>1</sup>Australian Museum, The Mesozoic Extinction Event, https://australianmuseum.net.au/the-mesozoic-extinction-event, (accessed September 2016).

<sup>&</sup>lt;sup>2</sup>USGS, Volcanic Ash Impacts and Mitigation, Mt St Helens 1980, https://volcanoes.usgs.gov/volcanic\_ash/mount\_st\_helens\_1980.html.

<sup>&</sup>lt;sup>3</sup>P. Taylor, O. Jagoutz, instructors, 12.001 Introduction to Geology, 16: Volcanoes, MIT Open Courseware, http://hdl.handle.net/1721.1/96863.

of the most recent meteor impact event, about 65 million years ago, and only some of the smaller flying dinosaurs, a few reptile species, and a new group of small, warm-blooded mammals, the distant ancestors of humans, were able to adapt and survive.<sup>4</sup>

On the earth's geological timeframe, with millions or even tens of thousands of years to change and restabilize, contamination is not all bad.

On a more human timeframe, well within a single lifetime, CO,  $CO_2$ , and acid emissions from relatively short-lived, sudden, geological shifts and eruptions can "naturally" create locally high atmospheric concentrations of contaminants that are toxic (harmful or deadly) to living creatures.

Wind, the natural, physical force of atmospheric movement, can contain sufficient energy to move particles, coarse PM, into the air from dry surface soils or sand. Intense wind events can create dust storms that themselves sandblast plants, animals, natural rock, and soil features, emitting more particles. Small liquid droplets of ocean spray that remain airborne and dry out also may become airborne particles of salt that, with other chemicals, continue to affect air quality. The smoke from wildfires can greatly reduce visibility over large areas.<sup>5</sup>

Human activities generate many of the same air contaminants that natural processes do. Fires set by people release similar emissions. Digging trenches and mining, farming, and transportation emit more dust particles than if the land is left untouched. Primitive cooking and heating fires, ovens, and furnaces release particles as smoke and traces of the fuel's unburned, carbon-based *hydrocarbons* (HC).

Biogenic emissions and liquid and solid wastes are created by human and other biological, life processes. People domesticated and fenced animals, concentrating their emissions. Inside animal digestive systems, including humans, enzymes and microbes operate in an environment without oxygen ("anaerobic") and generate methane and other reduced gases such as H<sub>2</sub>S.<sup>6</sup> Cows and pigs, ruminant animals with long, anaerobic digestive systems, generate detectable amounts of these odorous gases, ammonia, and several HC compounds in a group called *volatile organic* 

<sup>&</sup>lt;sup>4</sup>T.A. Hansen, C.F. Koch. (2017). Cretaceous Period Geochronology, Encyclopedia Britannica, http://britannica.com/science/Cretaceous-Period, (accessed January 12, 2017).

<sup>&</sup>lt;sup>5</sup>USEPA Office of Air Quality Planning and Standards, *Prescribed Burning Background Document and Technical Information Document for Prescribed Burning Best Available Control Measures*, p. 2-15, Research Triangle Park, EPA 450/2-92-003, 1992, https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=00001X20.PDF.

<sup>&</sup>lt;sup>6</sup>University of California, Berkley, Introduction to the cyano-bacteria, architects of earth's atmosphere, http://www.ucmp.berkeley.edu/bacteria/cyanointro.html, (accessed November 14, 2016). Cyano-bacteria use sulfur transfer for energy, with oxygen as a waste.

compounds (VOC). Similarly, anaerobic chemistry can occur in piles of dead or waste biological material where bacteria and other microorganisms decompose organic compounds, <sup>7</sup> creating solid and gaseous byproducts. Animals can detect many of these emissions with their odor sensor, a nose, or in the case of a snake, a tongue.

As settlements developed, growing demand for energy from wood, peat, and other accessible fuels produced increasing amounts of smoke. Piles of farmyard animal and other waste release decomposition gases, a recipe for creating an unpleasant local atmosphere. Horses and draft animals provided the most significant power for mobility on farms throughout most of human history. As resident beasts of burden in city settlements and on its roadways, the amount of waste they generated (and odorous VOC and TRS emissions) became locally significant.

Historic human activities for extracting and refining metals and other minerals required human and animal energy for crushing and high energy from fire for heating. These activities released dust from mining and crushing as well as combustion emissions from the ovens or furnaces melting the raw metal ores. They continue to be production processes emitting contaminants today.

# 2.2 THE INDUSTRIAL REVOLUTION – ITS ENERGY NEEDS AND PRODUCTS

Anthropogenic air emissions have increased rapidly since the dawn of the Industrial Revolution. The demand for energy to run industrial mills led to new combustion energy-producing processes emitting much more CO,  $CO_2$ ,  $nitrogen\ dioxide\ (NO_2)$ , and particulate smaller than 10 microns  $(PM_{10})$ . Coal, the energy rich, organic "rock" buried in the earth, was a better fuel than others growing in the forests and fields around settlements, and it answered the increasing demand for power. In addition to smoke, coal fuel also emits  $SO_2$ .

Processes for manufacturing paper, glass, chemicals, and building materials all emit large quantities of particles and fuel burning byproducts from the energy they use. New, synthetic chemical feedstocks and liquids, which evaporate, emit VOCs. A summary of the key emission sources is shown in Table 2.1.

<sup>&</sup>lt;sup>7</sup>N. Trautmann, and E. Olynciw. (1996). Compost Microorganisms, Cornell University, 1996, http://compost.css.cornell.edu/microorg.html, (accessed February 21, 2017).

Table 2.1. Key emissions and sources

Pollutant	Abbreviation	Key sources
Coarse particulate	PM	Volcanos, farming, mining, fires
Fine particulate	$PM_{10}$	Fires, other fuel combustion
Total reduced sulfur	TRS	Volcanos, biogenic, material processing
Hydrogen sulfide	$H_2S$	Volcanos, biogenic, material processing
Sulfur dioxide (gas)	$SO_2$	Volcanos, coal and oil combustion
Carbon dioxide	CO <sub>2</sub>	Volcanos, biogenic, fuel burning
Carbon monoxide	СО	Volcanos, fires, fuel combustion
Hydrocarbons	НС	Unburned fuel, synthetic carbon- based chemicals
Volatile organic compounds	VOC	Biogenic, evaporated fuel, petroleum evaporation and product use, solvents
Nitrogen dioxide (gas)	NO <sub>2</sub>	Boilers, engines, high temperature fires
Lead	Pb	Waste incineration, fuels containing lead and lead additives

## 2.2.1 THE PROCESS OF BURNING FUEL FOR HEAT, LIGHT, AND POWER

Humans have long burned plant-derived fuels in open fires, fireplaces, and simple stoves to produce heat and light. The combustion of a fuel with a flame, burning, is the chemical reaction process of adding oxygen to compounds, oxidation. Oxidizing plant-based organic fuels is exothermic and releases stored energy. In the atmosphere, the energy appears as light

or heat. The cellulose and other carbon molecules in wood and other plants can yield enough energy to maintain temperatures that sustain burning, but combustion and emissions also depend on the composition of the fuel and air supply of the fire. Organic, bioenergy fuels include peat, grasses, wood, dried manure, or other food and agricultural waste.<sup>8</sup>

"Open burning," a wildfire, bonfire, or fire in piles of wood or other solid materials, occurs at the standard pressure of the atmosphere ("ambient") and under air supply conditions created by wind and weather. Wind and air currents in the burning fuel, or forest, create different heat levels and pockets and dynamically change how atmospheric oxygen is supplied to an open fire. Fuel moisture, humidity, and, to some extent, *ambient* (natural, outdoor conditions) temperatures significantly affect the efficiency of combustion in the open and in simple fireplaces and stoves.

The organic (carbon based) compounds in wood and other solid fuels volatilize when heated, and these organic gas vapor molecules are chemically oxidized. All of these carbon-based fuels also contain quantities of minerals, which become ash particles. These PM can be carried up in the hot plume as fly ash, making smoke, but much of the ash is heavier, and it remains at the base of the burnpile.

Burning fuels with high moisture content is relatively inefficient at providing energy because a significant amount of the energy released is devoted to boiling the water. Plant fuels contain up to 50 percent water. When combustion efficiency decreases, PM is emitted at a higher rate in the plume of smoke from the fire. Open burning is relatively inefficient in producing useful energy compared with designed and contained combustion technologies like boilers and engines.

Plant material buried deep in the earth was converted to coal, petroleum, and natural gas in two main geologic eras of earth history some 300 million years and 100 million years ago. The carbon-based molecules of these plants were compressed into fossil compounds, which effectively stored energy from the abundant plant growth during those hot climate periods. After much of the water and oxygen were stripped out from the living biological chemistry during fossilization, these fuels have more energy density per weight than plants. Where there were local deposits of coal, as was the case in England and Wales, people burned

<sup>&</sup>lt;sup>8</sup>N. Krajnc. (2015). UN Food and Agriculture Organization, *Wood Fuels Handbook*, Pristina, 2015, http://www.fao.org/3/a-i4441e.pdf, (accessed July 17, 2016).

<sup>&</sup>lt;sup>9</sup>US DOE EIA, Oil: Crude and Petroleum Products Explained, http://www.eia.gov/energyex-plained/index.cfm?page=oil\_home, (accessed February 12, 2017).

coal in their homes for heating and cooking, replacing wood, peat, straw, and dung.

Because chemical compounds in plant carbohydrates and fossil fuel hydrocarbons are primarily carbon and hydrogen, combusting them generates  $\mathrm{CO}_2$  and  $\mathrm{H}_2\mathrm{O}$  emissions. Perfectly efficient fuel oxidation emits PM composed only of the noncombustible minerals in the fuel, but other byproduct gases are also emitted, even under the best combustion conditions.

Fossil fuels provide the primary source of energy today. The specific characteristics of coal and petroleum vary greatly—each geographic location and the conditions that created the fuel had a different mix of plants as raw material, and different pressures and geological conditions have compressed them. The heat content of different fuels differs, and therefore, a different amount or weight of fuel must be combusted to provide the same useful energy.

Bituminous coals contain the lowest fixed carbon and highest volatile carbon compounds, and anthracite coal contains more ash and energy per weight than bituminous coal. Most bituminous coals have more sulfur and nitrogen than anthracite coals. The soft coal, lignite, resembles its predecessor, peat. It contains the least energy per weight and may contain as much as 70 percent moisture. Coal generates more particulates and oxidized combustion byproducts than primitive fuels and emits more SO<sub>2</sub> and CO<sub>2</sub>. Burning coal in boilers emits more nitrogen oxides (NO, NO<sub>2</sub>), CO, and VOC than other fuels.

Coal resources were supplemented when reserves of energy dense, fossil petroleum liquids, and means of extracting them were discovered. Petroleum is a hydrocarbon compound liquid, "crude oil," used as the raw material for liquid fuels and other organic chemicals. As with coal, different geologic and geographic locations produce crude petroleum with very different compositions. Raw crude oils from different oil fields vary greatly in molecular weight, type of carbon compounds, and other trace constituents. Petroleum compounds contain carbon chain and ring compounds, some only as long as a few carbon atoms. Larger, carbon-based chemical compounds with higher molecular weights often do not evaporate as easily as the shorter, lighter ones, and they remain liquid or solid at ambient temperatures.

In oil refineries, the distillation process separates lighter oil fractions from other materials in crude oil. Distillation uses significant amounts of

<sup>&</sup>lt;sup>10</sup>Chemistry Explained, Coal, http://www.chemistryexplained.com/Ce-Co/Coal.html, (accessed February 12, 2017).

energy to boil off the lower molecular weight compounds from the rest of the oils.

Gasoline (petrol) is the lightest, liquid HC group distilled from petroleum. It is highly flammable, vaporizes at ambient temperatures, and ignites at  $-43^{\circ}$ C, explosively when ignited by a spark. The next heaviest, distilled compound from petroleum is diesel fuel, also known as #2 fuel, distillate, or heating oil. This low volatility oil is used widely in residential furnaces and small boilers, and has an ignition flashpoint of  $52^{\circ}$ C. It, like gasoline, contains little of the ash that ends up in the heavy residual oil products. Often, the distilled, oil fraction products are treated to remove contaminants, including sulfur. For more than 50 years, heating oil has been regulated so it contains no more than 0.3 to 0.5 percent sulfur. The sulfur restriction on transportation diesel fuel in the United States is 0.05 percent.

Heavy residual petroleum oil is left at the bottom of refinery distillation towers and contains increased concentrations of trace metals and heavy hydrocarbons. Residual oil, #6 oil and distillate/residual blends, are burned in large boilers in electric generating stations and industrial powerhouses. Residual oil has such low viscosity that it must be heated to flow into boiler burners. Other refinery "bottoms" include bitumen, tar, pitch, and asphalt, a semi-solid form of petroleum also found in nature.

Much of the conventional liquid fuel stock today is derived from catalytic cracking (splitting) the large carbon compounds in petroleum. Developed in the 1930s and 1940s, cracking is used to produce light, shorter-chain hydrocarbon products.

The other fossil fuel, "natural gas," has also been found in abundant quantities in deposits of coal, petroleum, and in separate, geologic gas fields. This gas contains more than 99 percent methane ( $\rm CH_4$ ), the simplest carbon compound. Such a simple molecule combines with oxygen easily, releasing energy without any fuel byproducts other than  $\rm CO_2$  and  $\rm H_2O$ . Extracting or processing natural gas also collects small quantities of other gaseous carbon molecules present in fossil fuel deposits with 2 to 6 carbons, ethane through hexane. <sup>12</sup>

Hydrogen gas can also be used as a fuel, but rarely found in deposits that could be extracted from nature. A fuel summary is found in Table 2.2.

<sup>&</sup>lt;sup>11</sup>Citgo, Safety Data Sheet, CITGO Gasolines, All Grades Unleaded, May 19, 2015, http://www.docs.citgo.com/msds\_pi/UNLEAD.pdf, (accessed February 21, 2017).

<sup>&</sup>lt;sup>12</sup>US Department of Energy (DOE), Energy Information Administration (EIA), Oil: Crude and Petroleum Products Explained, http://www.eia.gov/energyexplained/index.cfm?page=oil\_home, (accessed February 12, 2017).

Table 2.2. Fuel types and characteristics<sup>13</sup>

	Ash/Mineral content	Sulfur content	Nitrogen content		
Fuel	(% by wt)	(% by wt)	(% by wt)	Heat content	Moisture <sup>14</sup>
Wood <sup>15</sup>	1.0%	0.01-0.08%	0.13-0.5%	9,300–18,610 MJ/Mg	20–50%
Lignite	10–50%	0.4–1.0%	0.5-0.9%	9,300–19,310 MJ/Mg	<20%
Bituminous	3–12%	0.7–4%	0.5-2.0%	25,600–34,900 MJ/Mg	5-10%
Anthracite	10–20%	0.6–0.8%	1.0-2.0%	30,240-34,890 MJ/Mg	~5%
#6 residual oil <sup>16</sup>	0.2%	0.5-8%	0.3-1.2%	41.18 MJ/liter	Negligible
#2 distillate oil	negligible	0.05-0.3%	negligible	38.46 MJ/liter	Negligible
Gasoline	negligible	negligible	negligible	34.54 MJ/liter	Negligible
Propane	negligible	negligible	negligible	25.44 MJ/liter	Negligible
Natural gas	negligible	negligible	negligible	$38.38 \text{ MJ/m}^3$	negligible
Hydrogen <sup>17</sup>	none	none	none	119.6-141.6 MJ/kg	none
(1 kilowatt- hour)				0.2778 MJ	

<sup>&</sup>lt;sup>13</sup> USEPA, AP-42 Compilation of Air Emission Factors, https://www.epa.gov/air-emissions-factors-and-quantification/ap-42compilation-air-emission-factors.

<sup>&</sup>lt;sup>16</sup> M.R. Riazi. (2013). Characteristics of Heavy Fractions for Design and Operation of Upgrading Related Processes, Sulfur and <sup>15</sup> N. Krajnc. UN Food and Agriculture Organization, Wood Fuels Handbook, Pristina, 2015, http://www.fao.org/3/a-i4441e.pdf, <sup>14</sup> Professor Ljubisa Radovic, Pennsylvania State University, Chapter 7, Coal, http://www.ems.psu.edu/~radovic/Chapter7.pdf. (accessed July 17, 2016).

Nitrogen Contents of Heavy Oil ,2013 AIChE Annual Meeting, San Francisco, California, November 7, 2013, http://www3.aiche.org/ <sup>7</sup> U.S.Oak Ridge National Laboratory, Transportation Energy Data Book, Appendix B, http://cta.ornl.gov/data/appendix\_b.shtml, proceedings/content/Annual-2013/extended-abstracts/P346526.pdf, (accessed July 22, 2017). (accessed October 7, 2017). 13

#### 2.2.2 TECHNOLOGY FOR HARNESSING OR MAKING POWER

Tremendous advances in engineering, science, and invention provided a foundation for the Industrial Revolution. During the 18th century, inventors and engineers had begun to make use of steam energy when they developed ways to manufacture iron tanks and large metal containers that did not leak under pressure. Copper "boilers" had been used as early as the Greek and Roman empires, but new designs for boilers and other devices produced more useful heat energy than cook pots and traditional brewer's kettles. Industrial development in Europe and the United States, far from rivers and waterpower, could be powered by burning coal in a boiler to generate steam. Factories overwhelmingly chose coal as fuel for powerhouse equipment rather than wood. Coal was, and still is, transported from the mines to industries around the world.

In 1710, Thomas Newcomen invented a simple, coal-burning, steam "engine" that could pump water from coal mines. It employed a simple, atmospheric pressure vessel to make steam. The modern, more powerful and practical steam engine was invented in 1776, by refining the steam system design and the method by which the engine conveyed energy to its end use. A "High Pressure Tram Engine" was invented for a locomotive vehicle on rails in 1802, to transport coal out of the mines.<sup>18</sup>

Boilers and commercial and residential furnaces contain and control combustion and enable people to capture energy to transfer in the form of heat, steam, or hot water. The energy-releasing process of this type of equipment is called *external combustion*. These emission sources burn the fuel in a chamber and generally use separate air or liquid systems, independent of the combustion exhaust stream, to transfer heat energy for generating electricity, heating homes, and so on. Steam engine designs are external combustion processes, as well.

Designs to best harness the energy from boiler and engine equipment combustion rely on the composition and condition of the fuel as well as key parameters including the boiler firing method and heat transfer mechanism. <sup>19</sup> The design engineer's task is to ensure the fuel is available for complete oxidation for a sufficient time period, with good combustion conditions being a function of time, turbulence, and temperature, the three

<sup>&</sup>lt;sup>18</sup>Linda Hall Library. The Transcontinental Railroad: A History of Railroad Technology, http://railroad.lindahall.org/essays/locomotives.html, (accessed January 14, 2017). Richard Trevithick in 1802. Stephenson's "travelling engine" 1814.

<sup>&</sup>lt;sup>19</sup>USEPA AP-42, Chapter 1.1, Bituminous Boiler, 9/98, page 1.1-1, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s01.pdf.

"Ts." In general, as the efficiency of combustion increases, pollutant emissions decrease, with the exception of NO<sub>2</sub>.

The search for ways to reduce smoke from external combustion devices led to many advances in fuel preparation and feed technology in the early 20th century. The fuel feed systems for the oldest type of coal and solid fuel stoves, boilers, or furnaces use a shovel, a conveyor, or grate. In the U.S. patents for improved feed systems that pulverized-coal (PC) to burn in a boiler were granted in 1910, 1921, and 1922.<sup>20</sup> In the 1930s, better designs for both PC and oil fuels continued to reduce both smoke emissions and the slag that destroyed refractory material of boiler and furnace walls.<sup>21</sup>

Electric utility steam generator facilities and even much smaller, home oil and gas furnaces can capture heat energy at more than 90% efficiency.

The manufacture of large iron and steel tanks and piping also made it possible to collect, store, and distribute the newly discovered, energy dense, "liquid gold"—petroleum. People also developed means of using the natural gas found in deposits of coal or in underground gas fields. Petroleum products and natural gas soon brought light and heat to homes and businesses.

Transportation technology was revolutionized by coal and the steam engine. The first steam engine was installed in an ocean-going vessel in 1839. More expensive than oars or sails but relying on fewer workers, the promise of these engines became sufficiently practical, reliable, and fast to start to replace wind power. Steam replaced wind or horse and mule-drawn vessels along canals for riverway shipping and on iron railroads. By the second half of the 19th century, railroad carriage and track sizes had been synchronized. Not only coal but also other goods could be moved in any direction and brought to the grand new rail terminals to meet the energy demand of the city populations and industry.

New engine technologies to move smaller transportation vehicles were tried, both steam engines with small boiler systems and innovative internal combustion (IC) engine designs, which convert combustion energy directly into mechanical energy.<sup>22</sup> An IC engine using petrol (gasoline) can

<sup>&</sup>lt;sup>20</sup>W.R. Dunn. (1910). Mechanism for Feeding Pulverized Coal, Patent 954,944 Apr. 12, 1910, Patent Images, https://patentimages.storage.googleapis.com/pdfs/f3af524f97b9a532b4c8/US954944.pdf.

<sup>&</sup>lt;sup>21</sup>H.E. Witz, Pulverizer, March 22, 1927, Patent 1,621,571, Babcock & Wilcox Co, https://patents.google.com/?q=pulverized+coal&assignee=The+Babcock+%26+Wilcox+Company&scholar&sort=old.

<sup>&</sup>lt;sup>22</sup>USEPA AP-42, Chapter 3.3, Stationary Internal Combustion Sources, Gasoline and Diesel Industrial Engines, 10/96, https://www3.epa.gov/ttn/chief/ap42/ch03/final/c03s01.pdf.

recover 35 percent of the energy in the fuel, and theoretically, diesel-fueled engines can recover more than 50 percent.

IC engines became feasible and economically favorable as liquid storage containers were improved and new fossil fuels developed, as discussed in Section 2.3. The advantage of oil-fired engines over steam power for transportation quickly became evident. Steam locomotives gave way to diesel and petrol powered vehicles that did not need to operate on a track. Americans, and the rest of the world with access to petroleum fuels, accepted the new horseless buggies gladly. Engine power is often rated in *horsepower* units, equivalent to 2685 kilojoules (kJ).

#### 2.2.3 ELECTRIC ENERGY

Ben Franklin is well-known for his experiments with lightning, a kite and electricity, but Michael Faraday, in Great Britain, realized the utility of electricity when he developed the principal of the electric motor in 1821. Technology advances over the next half century engineered the means of generating a reliable supply of this exotic energy. Electricity offered alternatives to candle and gas lighting and horse-drawn municipal transit.<sup>23</sup> Electric motors could free factories from water power and still avoid smoke emissions. In 1882, Thomas Edison built the first electric power plant in downtown Manhattan, New York, using coal-fired steam boilers, and it generated enough electricity to light 400 lamps.<sup>24</sup> At least one company in the United States was designing and building hydropower dams in the 1880s to generate electricity, and it soon branched out into designing and building electric streetcars.

By the end of the 20th Century, fossil fuels were used in 95 percent of the U.S. power plant sources to produce both thermal and electrical energy. Nationally, more than 530 million megagrams (Mg) of bituminous and anthracite coal, nearly 205 billion liters of oil and 57 trillion cubic meters (m³) of natural gas were being burned in combustion sources. In 2015, 68 percent of the electricity generated in the United States was from coal, natural gas, and oil. The proportion of coal-based electric generation dropped to one-third of the total, much less than the proportion of 50 percent or higher in the years before 2010.<sup>25</sup>

<sup>&</sup>lt;sup>23</sup>Electrical Engineers Stone and Webster established an engineering firm to design electric systems.

 $<sup>^{24}\</sup>text{P.}$  Fusaro. Environmental Pioneer webcast, by Our Mark on the World, http://yourmarkontheworld.podomatic.com/entry/2016-10-19T04\_00\_00-07\_00.

<sup>&</sup>lt;sup>25</sup>US DOE EIA, Electricity Explained, Electricity and the Environment, http://www.eia.gov/energyexplained/index.cfm?page=electricity\_environment, (accessed December 2, 2017).

	1970	2015	2015 Total
Million Mg/yr	Combustion	Industry	Combustion
$PM_{10}$	2,871	negligible	922
$SO_2$	23,456	538	3,038
$NO_2$	10,061	1,280	3,182
CO	4,632	4,373	4,125
VOC	712	7,495	16,172

**Table 2.3.** U.S. Emissions: Total with Electricity and Recent Industrial (in million megagrams /year)

### 2.3 MATERIALS AND PROCESS EMISSIONS

Each material discovery and scientific innovation during the Industrial Revolution led to new inventions and production methods. Better methods for processing and refining metals from ores increased mining as well as metal and mineral production, and these processes emitted more PM and combustion contaminants. Smelting and furnaces for aluminum, iron, copper, zinc, and other metals operate at temperatures high enough to emit some of the metals in gas form, and therefore, those emissions also increased.

Mixers, kilns, and material handling to produce sand and gravel, bricks, clay products, and other construction materials emit PM and energy emissions. When a company manufactures chemicals such as lime, phosphate rock, acids, and agricultural fertilizers, it also produces PM and  $NO_2$  emissions. Thread and textile mills create dust PM from the friction of spinning and cutting cloth.

In 1709, coal was first processed into  $coke^{26}$  and added to pig iron during smelting, which produced steel. Coke production uses a process that drives volatile carbon compounds (VOC) and moisture from coal, and as a result, coke burns smokelessly. The process of making coke also leaves behind a tar that can be processed into many other chemicals. The stronger, more flexible iron alloy, steel, made from processing pig iron with coke, can be used to manufacture many other items, like tanks and piping.

Smokeless, indoor lighting fuel was brought to markets from the great age of exploration—whale oil. This high-quality oil could also be used in tanning leather and in cosmetics. However, by the end of the 18th century, advances in

<sup>&</sup>lt;sup>26</sup>O.C. Kopp, Professor Emeritus of Geological Sciences, Knoxville, TN, "Coal, Fossil Fuel", Encyclopaedia Brittanica, https://www.britannica.com/science/coal-fossil-fuel (accessed December 2, 2017). Coke was discovered by Abraham Darby.

chemistry yielded a competing energy source, synthetic gas produced from coal.<sup>27</sup> Coal gas, mostly methane, was also a clean-burning, smokeless fuel. Pipelines required impervious material with tightly connecting sections for transmission to homes and other buildings, and piping inside had to prevent gas leaks from building up and exploding. The coal gas plants themselves generated byproduct HC emissions that polluted the air and left behind solid waste with complex organic and metal compounds that polluted the soil and groundwater. The residual solid wastes left behind from the coal gas plants continue to pollute many historic, facility locations today.

Petroleum extraction and refining made major strides in the early 20th Century. Facilities with distillation towers produced useful commercial fuels for the new IC engines, as well as for boilers. Steel tanks replaced barrels and larger tanks made of wood and provided more effective management and the ability to ship larger quantities of oil fuels. The liquid heating and residual oils from refineries in the early 20th century made the economics of switching to new, fossil fuel-powered technologies and equipment even more favorable. Liquid fuels were well suited to power internal combustion engine technology once they could be stored in tanks small enough for mobile transportation applications.

The oil and gas industry collects, refines, and transmits oil and gas, which makes the pipelines and facilities a significant source of VOC emissions. It efficiently manages and contains the marketable petroleum products but is not as focused on conserving many of the byproduct VOCs and HC, which are easily released as emissions and wastes. Natural gas processing facilities emit HC, including methane. Thousands of miles of gas transmission pipelines emit HC from compressors and piping leaks. Containers and tanks in this industry and petrochemical manufacturing are emission sources due to evaporation or leaks.

The revolution in science and chemistry that accompanied and enabled the Industrial Revolution refined many natural compounds from the plant and animal world, but during the 1800s, chemists began to synthesize basic carbon chemical compounds without a biological feedstock. With the rise of textile mills, the demand for color dyes increased rapidly, and German chemists looking for new, permanent coloring agents created a plethora of synthetic chemical dyes. Many new compounds had a high enough vapor pressure to emit VOCs. Intermediary process compounds were volatile, too, and at the end of the process, a portion of the chemical products, or their coatings, would also be emitted.

<sup>&</sup>lt;sup>27</sup>William Murdoch invented the coal gas process in 1792.

<sup>&</sup>lt;sup>28</sup>Siddhartha Mukherjee, *The Emperor of All Maladies. A Biography of Cancer*, Scribner, 2010, p. 82.

Chemical industry facilities continue to develop and use liquid and solid organic compound feedstocks to produce synthetic organic materials and plastics. Ink and varnish manufacturers cook their intermediate products at temperatures up to 315°C. Paint and other coatings manufacturers disperse solid pigments into organic and water-based liquids to prepare them for application.

Nearly all facilities, including buildings, homes, assembly, and fabrication operations and small machine shops, clean or coat equipment and structural surfaces, and therefore, can emit significant amounts of VOC if the cleaning materials contain organic solvents. Food and electronics industry products require extensive cleaning processes. The storage containers for cleaners and degreasers are also potential VOC emission sources.

Specific industries and processes may emit other pollutants with specific hazards or previously unknown risks. *Hazardous air pollutants* (HAPs) may be solid PM or gases, and can be compounds either within the material being processed or created during the processing. The United States identifies nearly 200 compounds as HAPs today. Companies that use and manage liquid forms of some of these materials, like toluene and benzene, must reduce these VOC emissions to the extent practicable. Pesticides, leather tanning, and pharmaceutical industries have processes, some multi-step, that use a more diverse set of feedstocks and chemicals that may emit VOC and specific hazardous pollutants. Pulp and paper mills emit chlorine compounds depending on how they perform specific paper-making processes, such as bleaching paper.

Placing a slurry of *asbestos* (As) for insulation, or demolishing it for construction renovation, releases tiny, but elongated, asbestos fibers. Asbestos is also found in talc and vermiculite. Other well-studied, HAPs emissions identified before 1970 include benzene emitted from coking ovens, radiation-emitting particles (radionuclides), vinyl chloride, and arsenic.

Trace contaminants in fuels may become direct HAP emissions or toxic byproducts. *Mercury* (Hg), the quicksilver metal, is a constituent of many coals and is emitted from steam electric plants and boilers as a gas. The concentrations of many toxic contaminants in fuel are extremely low, but large quantities of coal and other fuels are burned and the emissions are significant. Coals from different areas contain and emit different amounts of Hg, chlorine compounds, arsenic, chromium, and Pb. Electricity generating units (EGU) emit a large proportion of the U.S. emissions of HCl, Hg, arsenic and HF, and the metals cadmium and chromium.

Elemental mercury was also refined and used in valve seals, thermometers, and pressure gauges and used as a catalyst by industries, such as the paper industry, to generate chlorine for production processes. In the 19th century, pure mercury was used extensively to make felt for hats. Wool fibers must be pressed together to make felt, and because mercury

is a very dense, heavy liquid at ambient temperatures, it was an excellent process material for compressing wool. Although release to the water is the most common path into the environment, it was a potential emission from various industries before it was eliminated from most products.

# 2.4 RELATING AIR QUALITY TO EMISSIONS AND EMISSION SOURCES

Humans have built a great number of emission sources since the Industrial Revolution began, and anthropogenic emissions have increased significantly. Air quality has improved in areas and countries where programs have imposed lower emission rates on smoke-stack facilities, *stationary sources*, and others. Emissions have been reduced significantly from the largest of these, *major sources*, including the EGUs, other large power facilities, metal and materials producers, and other large, industrial manufacturing plants. Permit systems requiring a new facility to have a lower emission rate than an older one provide for all new facilities to be cleaner, even though the annual tons of emissions may vary due to different production levels.

Broad-brush, material contaminant limits, like limits on the sulfur-in-fuel or paint VOC content, have reduced emissions from smaller *area sources* such as home heating systems, agricultural sources, the smaller, multiple area sources that may not have vent stacks. These emissions are tracked by the air pollution control agencies as a group by using metrics such as data on home heating oil sales or acres planted. Mobile source emissions are estimated as a group as well.

Air pollution control programs account for emissions by calculating and summarizing *emission inventories*, which can evaluate source contributions to air quality and show trends over time. Approved and accepted calculation methods generally account for emissions with an error margin of approximately 5 percent or less. The calculation methods for various source types are discussed further in Chapter 3.

The inventory data show the relative contribution of different types of emission sources. Agriculture and uncontrolled coal-burning EGUs contribute to the PM emissions significantly. The  $\rm NO_2$  emission inventory reflects the portion of emissions from electricity production and vehicles.

Today, international emission data records support a better understanding of global air quality. In addition to the U.S. records, the United Nations (U.N.) collects  $CO_2$  inventories from countries around the world.<sup>29</sup> The

<sup>&</sup>lt;sup>29</sup>United Nations (UN) Statistics Division, Datasets, FCCC Greenhouse Gas Inventory Data, http://data.un.org/Explorer.aspx?d=ENV.

**Table 2.4.** Global emissions -  $2010^{30}$ 

United (million Mg) States	United States	Russian Federation	Indonesia	Pakistan	Japan	China	Brazil	Nigeria	Global
Population 2010 (millions) <sup>31</sup>	309	143	242	185	128	1,338	199	159	6,857
$PM_{10}$	2,156	586	3,031	1,119	261	19,100	3,246	2,732	65,118
$SO_2$	10,106	2,630	1,994	8,569	1,114	29,989	1,201	201	102,442
$CO_2^{32} (10^9 \mathrm{Mg})$	6,116	2,057	1,995	329	1,083	9,713	1,484	462	45,768
00	19,388	;	:	!	1	77,707	;	;	1,076,752
VOC, NMOC	282	.199	739	141.2	119	8,974	654	009	13,343
$NO_2$	12,542	3,820	;	;	1,209	24,123	;	;	112,850

EUROPEAN COMMINSSION, JOHN RESCALCH CENTER, EMINSSION D'ARADASE TOI GROUAL AND RESCALCH (EDGAR) 22F 12000, IMMESSITES 1970 31 Census Bureau, World Populations, https://www.census.gov/population/international/data/idb/region.php?N=%20Results%20 2010, http://edgar.jrc.ec.europa.eu/overview.php?v=431.

&T=13&A=both&RT=0&Y=1970&R=-1&C=BR,CH,ID,JA,NI,PK,RS,US.

32 UN Framework Convention on Climate Change (UNFCCC), CO2 emissions excluding LULUCF/LUCF (offsets), http://data.un.org/ Data.aspx?d=GHG&f=seriesID%3aCO2.

**Table 2.5.** Emission changes since 1970<sup>33</sup>

	United States	ited States Russian Fed Indonesia Pakistan Japan	Indonesia	Pakistan	Japan	China	Brazil	Nigeria
$\mathrm{PM}_{10}$	3.3%	1%	2%	1.7%	1	29.3%	5.0%	4%
$\mathrm{SO}_2$	%6.6	3%	2%	8.4%	1%	29.3%	1	1
VOC, NMOC	2.1%	2%	%9	1.1%	1%	67.3%	2%	4%
$NO_2$	11.1%	3%	!	%0.0	1%	21.4%	!	!

33 European Commission, Emission Database for Global Air Research (EDGAR) 32FT2000v4.3, http://edgar.jrc.ec.europa.eu/ overview.php?v=431.

European Commission (E.C.) maintains international emission information for various studies in the Emission Database for Global Atmospheric Research (EDGAR), as shown in Tables 2.4 and 2.5.

The United States Environmental Protection Agency (EPA) has compiled and developed many reports and databases of emissions, control measures and monitored air quality. Peer-reviewed technical information on emissions and controls provides the basis for the EPA Air Quality Criteria publications and the New Source Performance Standards (NSPS), the national, U.S. emission limits for major sources. The first NSPS, in 1971, set emission limits for large, Fossil Fuel Steam Generators (EGUs), the category of sources in the United States with the highest emissions.

EPA also researches feasible emission reductions and standards for both existing and new sources to assure the control of HAPs, especially during start-up and malfunction shutdown events when emissions may exceed normal operating levels. A concise summary of the rationale and background for the air quality, NSPS, and NESHAPs standards can be found in the preamble of the U.S. Federal Register when the standards are published for comment. An additional summary of comments and final determinations precedes the rulemaking when the standard is *issued*, published as a final regulation, and takes effect.

### **CHAPTER 3**

## **AIR POLLUTANT EMISSIONS**

#### 3.1 EMISSION RATES AND AIR QUALITY

Human residences, agriculture, and transportation sources have released PM and other emissions for millennia, but since the mid-20th century, key contaminant emissions, as discussed in Chapter 2, have become widely recognized as *pollutants*. Pollutants can harm people and the environment, and they create nuisance and unwanted changes at various concentrations and duration. Polluted air has concentrations of these contaminants above the threshold concentrations; good air quality has pollutant concentrations below them.

#### 3.1.1 CRITERIA POLLUTANTS

The EPA Air Quality Criteria Reports present criteria for setting acceptable air quality concentrations in the ambient air, the outdoor public air-space, for PM and five other, polluting emissions—SO<sub>2</sub>, CO, NO<sub>2</sub>, VOC, and lead (Pb). The reports review and summarize the extensive scientific data for these *criteria pollutants* in detail.

The research information compiled in the criteria documents covers physical and chemical properties, exposure concentrations with associated effects on health, and concentration standards that protect health and avoid damage to materials, the environment, and the quality of life. It also includes the measurement methods used to obtain data, an overview of national emissions by source category, the earth environments affected by these pollutants, and potential emission control measures. These criteria are the basis for the U.S. *National Ambient Air Quality Standards* (NAAQS) and are updated periodically. Recently, PM criteria were updated, which led to a reduction in the NAAQS for PM<sub>10</sub> and PM<sub>2.5</sub>, with more attention to the latter. The United Nations Environmental Program

(UNEP) recommends ambient standards for the same pollutants for the international community, and many countries set ambient pollutant standards for their territories.<sup>1</sup>

The criteria pollutant that is not directly emitted is ozone  $(O_3)$ , which is a molecule created in the ambient air at significant concentrations when ultraviolet radiation energy from the sun causes photochemical reactions. Its concentration indicates how unhealthy the air quality is due to the mix of chemicals reacting. Air quality research in the mid-20th century investigated which pollutants were creating the dirty air and high  $O_3$  levels. The studies revealed that HC, VOC,  $NO_2$ , and other contaminants were input compounds involved in the reactions.<sup>2</sup>

By 1979, the criteria review designated the key, measurable pollutant in smog to be the oxidant  $O_3$  alone,<sup>3</sup> with the understanding that many kinds of reactive OC emissions are involved in the reactions that generate high, ambient  $O_3$  concentrations. Although the VOC set of HC and OC emissions is not itself a criteria pollutant, VOC emissions are also considered to be pollutants<sup>4</sup> and are restricted in the effort to keep  $O_3$  at acceptable concentrations. The main processes generating and releasing pollutants are summarized in Table 3.1.

#### 3.1.2 AIR POLLUTION CONTROL PROGRAMS

A combination of methods and data has to be used to create effective strategies and programs to achieve and preserve air quality as clean as the NAAQS, or cleaner. As described in this chapter, program planners and staff need to develop:

- a. baseline air quality pollutant concentration data
- b. monitoring networks for continued data collection

<sup>&</sup>lt;sup>1</sup>European Commission, Environment, Air Quality Standards, http://ec.europa.eu/environment/air/quality/standards.htm, (accessed June 26, 2017).

<sup>&</sup>lt;sup>2</sup>US EPA, 40 CFR Part 10, National Primary and Secondary Ambient Air Quality Standards, Notice of Proposed Standards for Sulfur Oxides, Particulate Matter, Carbon Monoxide, Photochemical Oxidants, Hydrocarbons, and Nitrogen Oxides, Federal Register, Volume 36, No. 21, Saturday, January 30, 1971. pages 1502 et seq. (36FR1502), https://www3.epa.gov/ttn/naaqs/standards/so2/previous/fr-1971-jan30-co\_phchemoxids\_hcs\_no2\_pmproposal.pdf. 
<sup>3</sup>US EPA, Table of Historical Ozone National Ambient Air Quality Standards (NAAQS), https://www.epa.gov/ozone-pollution/table-historical-ozone-national-ambient-air-quality-standards-naaqs, (accessed June 13, 2017).

<sup>&</sup>lt;sup>4</sup>The official US EPA VOC list is at 40 Code of Federal Regulations Part 51.100(s). The official list of VOC chemicals is defined by whether the specific compound participates in smog and ozone creation in ambient air. It excludes methane, ethane, chlorinated or other halogenated organics, and others.

Table 3.1. Key air pollutants and emission processes

Pollutant		State/Phase	Comment	Key sources
Particulate	PM	Solid		Construction activities, vehicle engines, fires, burning, agriculture
Total Suspended Particulate	TSP		< 45 µm	
Coarse, inhalable particulate	$PM_{10}$	Solid	$<$ 2.5–10 $\mu m$	Combustion, fires, mineral products, agriculture
Fine Particulate	$PM_{2.5}$	solid, liquid	<2.5 μm	Combustion, fires
Fine Particulate		Solid	Metal constituents	Mineral production, contained in PM
Sulfur dioxide (gas)	$\mathrm{SO}_2$	Gas	Can oxidize to SO <sub>4</sub> (solid, PM <sub>2.5</sub> )	Combustion of sulfur containing fuels, processing minerals, and materials containing sulfur
Nitrogen dioxide (gas)	NO <sub>2</sub>	Gas	Can oxidize to NO <sub>3</sub> (solid, PM <sub>2.5</sub> )	Combustion, including vehicle engines
Hydrocarbons/ Organic Compounds	OC 0C	Gas	Can oximize to $CO_2$ (gas) HC compounds are primarily organic; made of H and C.	Combustion, including venicle engines. Unburned and evaporated fuel, solvents and waste gas.
Non-methane OC	NMOC	Gas	The subset of OC and HC without methane	Petroleum/gas production, chemical manufacturing, landfills
Volatile OC	$VOC^5$	Gas	A subset of OC that reacts in the air	Petroleum evaporation, volatile liquid use and storage, tanks
Lead	Pb	Gas, solid		Marine vessels, leaded fuel, paint, old pipes and batteries, lead-containing products.

<sup>5</sup>VOC is also called Reactive Organic Gases, (ROG) or Precursor Organic Compounds (POC) by some air programs.

- c. emission rate data from stack testing and other studies
- d. emission inventories of criteria pollutants
- e. knowledge about sources and emission rates of other toxic air contaminants harmful to the environment

Further information and measures needed for good air quality management are:

- a. programs that can require sources to control process emissions and enforce permit or regulatory requirements, in Chapter 5
- b. tools to relate emissions to ambient concentrations, along with more monitoring information, in Chapter 6

Before 1970, only a few ambient monitoring stations were collecting air quality concentration data, which means it was not possible to know the precise location, timeframe, and extent of air pollution.

Air programs in the United States and around the world now maintain networks of real-time monitors to determine ambient pollutant concentration data throughout the year. Ambient concentrations of each pollutant need to be compared with acceptable concentrations for appropriate time periods to determine if air quality in the area meets the ambient standards. Where a pollutant concentration is too high, the sources contributing those emissions must be identified, with the rates and timeframe of emissions, in order to plan feasible and effective emission reductions.

Accounting for all sources and emissions to the environment in an emission inventory provides a pollutant baseline. The kilograms of emissions in an hour or a day create the air quality concentrations over the short term. Over the course of a year, the tons of emissions relate to the annual average concentration standards for NO<sub>2</sub> and PM. Regular annual inventories in megagrams (Mg, metric tons, 1,000 kilograms) per year also identify the largest sources and help to assure that air quality will not deteriorate.

Direct emission testing in the source exhaust plume provides the best, quantitative release rate information for process equipment with a vent or stack, but only for that individual source at its operating conditions during the time period tested. By the 1960s, emission rate testing had been done for boilers, automobiles, and equipment in a few miscellaneous industries. A robust set of results were available for PM and some other combustion emissions, because PM has always been a factor in air pollution, especially from boilers. However, little reliable, quantitative information on most other emission sources was available until air programs and permits required more large emitters to test emission rates. With the new test data,

more complete, quantitative information on exhaust emission concentrations has been produced.

Information and data on processes and emissions provide a basis for setting permissible emission rates as *emission standards* (limits) for each category of regulated sources. Scientists and engineers at the EPA, in academia, in industry, and at state and local air quality agencies around the world continue to test and do research on how processes generate, release, and control criteria pollutants and *hazardous air pollutant* (HAP) emissions. By using test data and engineering knowledge of the processes creating emissions, studies have determined typical rates of emissions from categories of processes producing similar products, such as energy generation or steel production.

Air agencies control air pollution most effectively at its source, using emission standards, which is the main approach to implement programs to achieve the NAAQS. Source emission limits in regulations or facility permits can drive emission reductions for individual HAPs as well as the one other criteria pollutant, CO<sub>2</sub>, which have no NAAQS. Source emission standards are enforceable through emission limits for nationally important equipment categories. The EPA *New Source Performance Standards* (NSPS) and *National Emission Standards for Hazardous Air Pollutants* (NESHAP) must be implemented by state and local air agencies and are described further in Chapter 5. In addition, other agencies adopt source limits in their own regulations and can incorporate emission standards for specific sources and pollutants in individual source permits.

The toxicity of the criteria pollutants was addressed on a national level in the first national United States air program, but only seven HAPs were regulated. The metals Hg and beryllium are HAPs, as are arsenic, benzene, and asbestos. These pollutants are not found at significant concentrations everywhere in the ambient air, but are important locally, near their emission sources. Starting in 1970, Hg emission limits were imposed on ore processing, wastewater sludge incineration, and mercury cell chlor-alkali plants. When more sensitive Hg emission monitoring methods were developed, the mass emissions from burning coal and from waste combustors were found to be a significant portion of the remaining Hg emission inventory. The EPA then required large, coal-fired electric plants and waste combustors to install capture systems to reduce emissions of this HAP.

#### 3.1.3 EMISSION RATES AND INVENTORIES

Air management agencies calculate emission quantities from each kind of source in an air basin, large and small, to produce comprehensive emission

inventories and to understand the burden of each criteria pollutant on local air quality. They base the inventories on reports from major sources and on resources such as EPA *AP-42: Compilation of Air Emission Factors* (AP-42).<sup>6</sup> AP-42 describes how processes generate emissions, the technologies applied to control them, and the emission rates. A good reference for estimating and calculating source emission quantities, AP-42 summarizes testing, research, and emission studies for each source category with similar emitting processes and levels of activity or production. Detailed information and data from the studies are included in a series of background documents.

The *emission factors* (EFs) presented in AP-42 convert test information on emission rates for each kind of process into "a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant . . . Factors are usually expressed as the weight of pollutant divided by a unit weight, volume, distance, or duration of the activity emitting the pollutant (e. g., kilograms of particulate emitted per [megagram] of coal burned)."

An EF reflects how much pollution is emitted per work done, an average for a given process type, and it shows how clean the process of a specific facility is with respect to emissions. EFs can be different for large and small emission sources operating similar equipment, even those using similar fuels or raw materials, if the size of the unit changes the process conditions that generate emissions. For example, EFs for a utility steam boiler firing natural gas are not the same as EFs for a gas-fired heating furnace in a home. Test data represent emission concentrations at a point in time, but EFs are standardized to the fuel input or production rate and allow comparison of equipment doing the same kind of work, with different capacity and process designs. EFs developed for steam electric generator units (EGUs) and other combustion sources have the highest level of confidence. Fuel and design categories of combustion devices can be segregated and evaluated.

Example EFs for two processes are presented below in Table 3.2 with an explanation of the general emission calculation methods. Further discussion of EFs for specific pollutants and processes is found in Section 3.2.2 and later sections.

<sup>&</sup>lt;sup>6</sup>US EPA, Air Emissions Factors and Quantification, *AP-42, Compilation of Air Emission Factors*, https://www.epa.gov/air-emissions-factors-and-quantification/ap-42-compilation-air-emission-factors, (accessed November 2016 through July 2017).

<sup>&</sup>lt;sup>7</sup>R.L. Duprey, ed. PHS Pub No. 999-AP-42, First Edition, Washington, DC, 1968, https://www3.epa.gov/ttn/chief/ap42/oldeditions/1st\_edition/ap42\_phs\_1968.pdf. (Based on 1965 PHS compilation of Combustion Gasoline evaporation and Selected Industrial Processes).

Pr	ocess	Units	PM <sub>10</sub>	SO <sub>2</sub>	CO <sub>2</sub>	$NO_2$	CO	VOC
a.	Pulverized Coal Boiler	kg/Mg coal burned	9.10	38.00	3020.0	15.50	0.25	0.02
b.	Coal-fired brick kiln	kg/Mg bricks produced	0.68	0.26	150.0	0.40	0.60	0.012

**Table 3.2.** Example coal boiler<sup>8</sup> and brick kiln<sup>9</sup> emission factors

kg: kilograms; Mg: metric tons, 1,000 kg

Boilers of the first listed process type, (a) in Table 3.2, burn pulverized coal (PC), and these specific emission sources are designed with "wet" combustion chamber bottoms. The EF relates the kilograms of emissions to each Mg of bituminous coal burned. Both the PM<sub>10</sub> and SO<sub>2</sub> EFs are based on equations that use fuel characteristics, the ash and sulfur content. The formulae for the EFs presented in Table 3.2, 1.3xA (ash) and 19xS (sulfur), assume that the coal quality is in the midrange of bituminous coals—7 percent ash and 2 percent sulfur. The EFs are the same for all PC boiler facilities with generating capacity over 21 MW using the same type of coal, which means the larger and smaller boilers in this range are as clean as each other and have the same pollutant emission rates.

The second process, (b), a brick drying and tempering kiln that fires coal, is one of several operations in Brick Manufacturing and is normalized for the quantity of bricks produced.

To calculate emissions using an EF:

 $EF \times activity level for time period = mass emissions for time period$ 

Table 3.2 presents the calculation for hourly emissions of a 30 megawatt (MW) PC boiler, which uses 3.9 Mg bituminous coal at capacity:

 $PM_{10}$  Emissions: 9.1 kg/Mg coal  $\times$  3.9 Mg burned/hour = 311 kg  $PM_{10}$ 

 $SO_2$  Emissions: 38 kg/Mg coal  $\times$  3.9 Mg burned/hour = 1300 kg  $SO_2$ , and so forth.

<sup>&</sup>lt;sup>8</sup>US EPA, AP-42 Chapter 1.1 Bituminous and SubBituminous Coal Combustion, 9/98, page 1.1-1, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s01.pdf.

<sup>&</sup>lt;sup>9</sup>US EPA, AP-42 Chapter 11.3 Brick and Structural Clay Product Manufacturing, 8/97, https://www3.epa.gov/ttn/chief/ap42/ch11/final/c11s03.pdf.

It is important to understand that although the emission rates are the same for both large and small PC boilers with capacity over 21 MW, if both operate all year, around the clock, very different quantities of emissions will be released to the environment.

The calculated emissions of a brick kiln for a factory manufacturing 1,000 Mg of brick are for the period of production:

$$PM_{10}$$
 Emissions: 0.68 kg/ Mg bricks produced  $\times$  1,000 Mg = 680 kg  $PM_{10}$ 

 $NO_2$  Emissions: 0.40 kg/Mg bricks produced  $\times$  1,000 Mg = 400 kg  $NO_2$ 

The boiler emissions in Table 3.2 are presented as emissions per hour, and the emissions in Table 3.3 are the number of Mg emitted per year. Even though both charts show the emission loads to the air in units of mass (kg and Mg) and they are different, it is helpful to consider the *emission rate* of these boilers to be the same, in kilograms of emissions for each Mg of coal. By thinking in terms of emission *rates*, equipment and sources can be compared to see how clean they are for the work done. Source emission standards by EPA are always presented as emission rates, and can be expressed in work done or the equivalent concentrations in exhaust plumes as corrected for temperature and oxygen content.

The EF for PM<sub>10</sub> emissions from a boiler with a different burner design, an industrial size, tangentially fired coal boiler, is only 10 percent of the EF for the PC, wet-bottom boilers in Tables 3.2 and 3.3. <sup>10</sup> The direct emissions for a tangential boiler combusting the same amount of coal in a 30 MW or 200 MW boiler for 8760 hours per year would only be

Mg Emitted per year	Size	PM <sub>10</sub> (Mg)	SO <sub>2</sub> (Mg)	CO <sub>2</sub> (Mg)	NO <sub>2</sub> (Mg)	CO (Mg)	VOC (Mg)
Pulverized coal, wet bottom	30 MW	311	1,299	100,823	530	9	1
Pulverized coal, wet bottom	200 MW	2,098	8,760	696,158	3,573	58	5

Table 3.3. PC boiler emissions

<sup>&</sup>lt;sup>10</sup> US EPA, AP-42 Chapter 1.1 Bituminous and Sub Bituminous Coal Combustion, 9/98, page 1.1-1, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s01.pdf.

10 percent of the emissions of the same capacity PC boiler. In other words, the calculated, annual  $PM_{10}$  emissions of a 200 MW tangential (or cyclone) design boiler would be 209 Mg, rather than 2,098 Mg.

In addition, boilers of the same burner type with more efficient design, using less coal to produce the same amount of power or steam, have lower PM, CO<sub>2</sub>, and SO<sub>2</sub> emission rates per heat input and electricity produced. Boilers that are part of a combined heat and power (CHP) system emit less pollution per output than stand-alone boilers of the same design. In general, if similar equipment uses less fuel or process material for the same energy generation or production output, it will be a cleaner source of all pollutants. However, NO<sub>2</sub> and CO emissions from combustion equipment designed for efficiency may not always be lower, for reasons described in Sections 3.3.1 and 3.3.2.

Between 1968, when the First Edition of AP-42 was issued, and the 5th Edition in 1995, EPA published new information about emission rates and factors in regular updates and supplements. So much more test information has become available that EPA now maintains an online database of emission rates and EFs of both criteria pollutants and HAPs, WEBFIRE<sup>11</sup> (Factor Information Retrieval System), which is the up-to-date version of AP-42. Documents and studies of processes, emissions, and controls can be accessed through EPA webpages on CAA Standards and Guidelines. Another helpful resource for energy emissions is the Energy, Engines, and Combustion webpage, <sup>12</sup> which organizes links to AP-42, the New Source Performance Standards and Emission Guidelines. The linked references have typical emission rates for each process category according to fuel or material use and size of source.

Air quality programs collect not only emission test information from *major sources* in their area, those which emit more than a threshold quantity of emissions in a year, but also gather reports on fuel use and other process parameters. To determine emissions of the larger stationary sources, every U.S. program requires these facilities to submit fuel use and other activity level information on a periodic basis. Emissions can be summed up to review compliance with permit limits and trends in air quality. The detailed emission data are combined with calculated emission estimates for other sources to inventory total emissions within the entire area.

Emission processes and source categories can be organized into a few simple groups or more detailed ones. The United States has grouped

<sup>&</sup>lt;sup>11</sup> US EPA WEBFIRE EF database, https://cfpub.epa.gov/webfire, (accessed January 11, 2017).

<sup>&</sup>lt;sup>12</sup> https://www.epa.gov/stationary-sources-air-pollution/clean-air-act-standards-and-guidelines-energy-engines-and, (accessed March 17, 2017).

stationary (built), emission sources and processes into five main groups in an index of codes called the source classification codes (SCC). Three of these top five process codes are related to fuel use. Much of the information on EFs and research on process emission rates is mapped to these classification codes. The EPA uses nearly 10,000 valid, four-level codes, and the code lists can be found on the Emission Inventories website. The emission inventory reporting webpage of several state agencies includes a link to a searchable spreadsheet of SCC codes, including Massachusetts and Louisiana.

The second level of the code is the industry sector of the emission source. The third and fourth levels designate the type of input material or fuel and equipment.

In the example, the wet-bottom, PC boiler in Tables 3.1 and 3.2 falls into the Level 1 SCC group for external combustion. Adding SCC Level 2, the three digit code 1-01 shows this is a large, steam electric-generating station. Level 3 in the full SCC of 1-01-002-01 for this PC boiler indicates the fuel is bituminous coal (002), and Level 4, the PC wet-bottom configuration. If a burner design of a boiler at another electricity generating source burning bituminous coal was a cyclone style, only the fourth level code number for that process would be different (-03).

In SCC Category 3, Industrial Processes, coal mining and cleaning are included under SCC 3-05-010. A summary of the SCC structure is presented in Table 3.4.

In the past few decades, more attention has been put into mobile, agricultural, and residential emission estimates. More emission factor calculations and inventories of these source groups have been developed, as air quality programs and planners have come to understand the regional and global impact of air emissions.

The total emission inventory numbers for anthropogenic emissions in the United States show plainly that fuel combustion produces the most emissions, more than 80 percent of the NO<sub>2</sub> and SO<sub>2</sub> (Table 3.5). The predominance of energy production is most pronounced in the emission inventories of industrialized nations. Fuel combustion in transportation vehicles emits large quantities of NO<sub>2</sub>, VOC, and CO<sub>2</sub> and is usually inventoried in a separate category from stationary energy sources. Industrial emission sources contribute significant quantities of emissions, and other categories of human-created sources usually represent smaller portions of total emissions.

Worldwide, air quality programs develop emission inventories in similar but slightly different sets of categories. The international community now tracks emissions from energy generation and other sources. The Joint

<sup>&</sup>lt;sup>13</sup> US EPA, Source Classification Codes (SCCs), https://ofmpub.epa.gov/sccsearch/.

(continued)

Table 3.4. Overview of Source Classification Code (SCC) structure

Level 1: main type of process	Level 2: combustor size or industry	Level 3: fuel or material	Level 4: equipment design or process	Complete SCC
Boilers and other external combustion equipment	01 – Steam Electric Generator.	002 - Bituminous/ Subbituminous Coal	01 - Pulverized Coal: Wet 1-01-002-01 Bottom	1-01-002-01
	01	002	02 – Pulverized Coal: Dry 1-01-002-02 Bottom	1-01-002-02
	01	004 – Residual Oil Grade 6 Oil:	04 – Tangential Firing:	1-01-004-04
	02 – Industrial	002 – Bituminous/ Subbituminous Coal	01 – Pulverized Coal: Wet 1-02-002-01 Bottom	1-02-002-01
	03 – Commercial			
2. Internal Combustion Engines	01 – Electric Generation 02 – Industrial 03 – Commercial 04 – Engine Testing			
3. Industries	01 –Chemical Manufacturing	001 – Adipic acid	03 – Cyclohexane Oxidation	3-01-001-03

Table 3.4. (Continued)

Level 1: main type of process	Level 2: combustor size or industry	Level 3: fuel or material	Level 4: equipment design or process	Complete SCC
		Ammonia production	Primary Reformer: Natural Gas Fired	
	03 – Primary Metal Manufacturing	006 – Ferroalloy, Open Furnace	006 – Ferroalloy, Open 01 – 50% FeSi: Electric Furnace Smelting Furnace	3-03-006-01
		009 – Steel Manufacturing	03 – Basic Oxygen Furnace: Open Hood-Stack	3-03-009-03
	07 – Pulp and Paper and Wood 001 – Sulfate (Kraft) Products Pulping	001 – Sulfate (Kraft) Pulping	02 – Washer/ Screens	3-07-001-02
4. Petroleum and solvent				

<sup>+.</sup> remoteum an evaporation

5. Waste disposal

EPA, "Source Classficaton Codes (SCCs)," https://ofmpub.epa.gov/sccsearch/

**Table 3.5.** Inventory of selected U.S. pollutants by key source category (2014)<sup>14</sup>

Pollutant	PM	NO <sub>2</sub>	SO <sub>2</sub>
Source Category	$Mg \times 10^3$	$Mg \times 10^3$	$Mg \times 10^3$
Fuel comb. elec. util.	207	1,555	2926
Fuel comb. industrial	295	1,079	596
Fuel comb. other	334	485	119
Chemical & allied product manufacturing	18	42	104
Metals processing	53	68	98
Petroleum & related industries	33	746	93
Other industrial processes	705	306	156
Solvent utilization	4	1	0
Storage & transport	61	5	3
Waste disposal & recycling	277	103	33
Highway vehicles	281	4,238	26
Off-highway	181	2,540	69
Miscellaneous	0	158	72

Research Centre of the European Commission develops methods for and has compiled an Emissions Database for Global Atmospheric Research (EDGAR) that covers PM, acidifying gases, atmospheric warming gases including CO<sub>2</sub>, and OC halogen compounds or those that contribute to photochemical reactions.<sup>15</sup> The United Nations Task Force on National Greenhouse Gas Inventories Programme (NGGIP), a subgroup of the International Panel on Climate Change (IPCC), has also published methodologies, software for developing national inventories, and an Emission Factor Database for preparing CO<sub>2</sub> inventories.<sup>16</sup>

<sup>&</sup>lt;sup>14</sup>US EPA National Emission Inventory, 2014, https://www.epa.gov/air-emissions-inventories/national-emissions-inventory-nei, (accessed January 14, 2017).

<sup>&</sup>lt;sup>15</sup>European Commission (EC), Science Hub, EDGARv4 Methodology, http://edgar.jrc.ec.europa.eu/methodology.php, (accessed April, 23, 2017).

<sup>16</sup> UN, Simon Eggleston, Leandro Buendia et al, 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Institute for Global Environmental Strategies (IGES) for the IPCC, ISBN 4-88788-032-4, http://www.ipcc.ch/publications\_and\_data/publications\_and\_data\_reports.shtml#4.

Programs also use one more planning tool—models—to simulate plume dispersion and photochemical reactions, as further discussed in Chapter 6. The emission dispersion simulations allow a program to understand the relationship between the emission inventories and the source emission rates that contribute to ambient air quality concentrations and standards exceedances.

### 3.2 PM - SOLID EMISSIONS

PM has always been known as a cause of air pollution, especially PM emissions from combustion.<sup>17</sup> "Smoke" is the common term for high PM concentrations in an exhaust stream from a fire or emission stack. PM is obvious because it can be seen with the naked eye. Although airborne, the tiny, solid particles are visible in the atmosphere because light cannot pass through them, and they create opaque areas. Dust particles are eventually deposited by gravity from the air.

Even tiny liquid droplets block light and are defined as particulates. The best evidence of liquid particles creating visual opacity is water droplets—clouds or the steam from a cup of coffee. However, water is not defined as an air pollutant because it is a natural part of the atmosphere, water cycle, and weather, rather than a contaminant that causes health or environmental effects at threshold concentrations.

Scientific studies show that three size ranges of *total suspended particulate* (TSP) are important in air pollution. PM size is calculated as an effective diameter or *Mass Median Aerodynamic Diameter*. <sup>18</sup> The larger particles are usually generated and released by mechanical processes in a variety of shapes, usually angular. TSP includes particles 45 microns ( $\mu$ m) and smaller, because solids larger than this, with large aerodynamic diameters, do not become or stay airborne over any significant distances. For reference, the thickness of a human hair is about 70  $\mu$ m. <sup>19</sup> The smallest of the mechanically generated particles in the air is approximately 5  $\mu$ m.

Studies of PM since the 1950s have investigated the polluting characteristics and acceptable concentrations. The human nose filters out TSP  $> 10 \,\mu m$ . Air quality standards have been based on PM<sub>10</sub> rather than TSP

<sup>&</sup>lt;sup>17</sup> US EPA, Particulate Matter Pollution: Basics, https://www.epa.gov/pm-pollution/particulate-matter-pm-basics, (accessed November 25, 2016).

<sup>&</sup>lt;sup>18</sup>US EPA Particulate Matter Criteria Document, 1982, https://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=46205, (accessed March 14, 2017).

<sup>&</sup>lt;sup>19</sup> US EPA, Particulate Matter Pollution: Basics, https://www.epa.gov/pm-pollution/particulate-matter-pm-basics, (accessed November 25, 2016). A micron (μm) is 10<sup>-6</sup> meters, <0.0012 inches.</p>

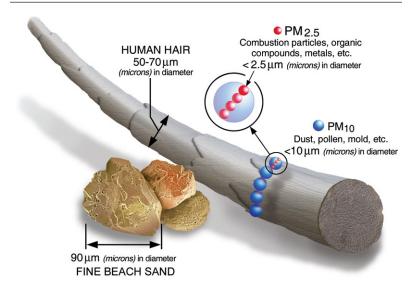


Illustration 1: US EPA, Particulate Matter Pollution: Basics, https://www.epa.gov/pm-pollution/particulate-matter-pm-basics

since the 1960s. A significant subset of  $PM_{10}$ , Fine  $PM_{10}$ ,  $< 2.5 \, \mu m$  in effective diameter ( $PM_{2.5}$ ), is differentiated from total  $PM_{10}$  because the particles are so small that they are only randomly released from the lungs with each breath. The weight of PM does not correlate directly with parts per million by volume (ppmv) concentrations due to the specific chemical composition of each particle. "Primary" PM is emitted directly as the result of the process generating it, as described below. "Secondary" PM is created from gas emissions by subsequent chemical or state changes in the atmosphere and is discussed in Section 3.5 of this chapter.

#### 3.2.1 ACTIVITIES MAKING DUST

Processes of human civilization, like farming, create dust particle emissions, PM or TSP. Feet and wheels on dirt paths and roadways kick up dust, especially when conditions are dry. Tilling a field breaks up the soil, and the wind can blow the dust into the air.

Other human mechanical processes emit large PM directly, while creating desired products. Grinding will shape or make smaller solid materials, such as polished marble, deburred metal parts, or flour. The mechanical processes of mining, cleaning, and sizing soil and minerals emit PM. To extract elemental metals, mineral ores containing them are mined, transported, and crushed, heated, or chemically treated. Transportation, crushing, and sorting processes also emit PM.

For example, coal mining and cleaning emit significant quantities of PM in the 10 to 30  $\mu$ m range as well as some coarse particulate, PM<sub>10</sub>. In surface coal mines, <sup>20</sup> mechanical overburden movement, grading, and storage pile emission rates depend on the process and activity level:

- a. size of the area blasted, bulldozed, or graded
- b. silt content of the minefield roads, overburden soil, and the coal itself
- c. the coal and soil ash moisture content
- d. the shape and duration of storage piles
- e. truck loading, unloading, and transit protocols or procedures

The emissions for industrial coal handling activities, transport, handling, grinding, cleaning, and drying, may be as much as 28 kg/Mg of coal processed.<sup>21</sup> Wood residue fuel preparation and handling have fewer PM emissions, other than the haul road dust.

Demolition of built structures or soil and rock formations releases PM. $^{22}$  Some construction materials, often those processed or manufactured in liquid form, create dust when broken up—for example wallboard, roof shingles, plaster, and asbestos. Asbestos, a natural mineral, is a particle with very specific pollutant qualities. The fibers can be longer than  $10~\mu m$ , but they are so thin and light that they can remain airborne. Asbestos fibers are a HAP. Introduced to the lung, they are *toxic*—poisonous to humans and animals.

Many emission control measures and technologies significantly reduce emissions from the exhaust vents of dust-producing processes and industries, and some EFs are available for the controlled emission rates. However, this book does not address PM controls or EFs for sources using them.

## 3.2.2 PM FROM ENERGY-GENERATING PROCESSES AND INDUSTRY

Fires emit smoke. Whether it is a wildfire started by a lightning strike or humans lighting fire for heat, cooking, light or protection, the primary contaminants emitted by combustion of carbon-based fuels are similar. The density and color of the visible emission plume will vary, depending on the specific fuel that is being burned and the combustion conditions.

<sup>&</sup>lt;sup>20</sup> US EPA, AP-42 Chapter 11.9, Western Surface Coal Mining, coal cleaning, 10/98, https://www3.epa.gov/ttn/chief/ap42/ch11/final/c11s10.pdf.

<sup>&</sup>lt;sup>21</sup> US EPA, AP-42 Chapter 11.10, Coal cleaning, 11/95, https://www3.epa.gov/ttn/chief/ap42/ch11/final/c11s10.pdf, https://www3.epa.gov/ttn/chief/ap42/ch11/final/c11s11.pdf (conversion to gas).

<sup>&</sup>lt;sup>22</sup> US EPA, National Emission Inventory, 2014, https://www.epa.gov/air-emissions-inventories/national-emissions-inventory-nei, (accessed January 2014, 2017).

If the PM emission rate is high, the particles in the plume can make it completely opaque, blocking all light. A plume can appear very dark, especially if the PM is composed of black carbon soot from the incomplete combustion of organic fuels.<sup>23</sup> Lighter, hazier smoke, with lower opacity, indicates the exhaust plume has fewer particles.

Both open fires and fuel combustion equipment, such as boilers, emit PM. Open burning has a high, primary PM emission rate. Wood and other plant-derived fuels, including peat, grasses, dried manure, and fossil fuels, contain small amounts of minerals, which cannot not burn or oxidize. More than 90 percent of uncontrolled wood fire smoke emissions are  $< 10 \, \mu m$  in diameter, and most forest fire emissions are PM<sub>2.5</sub>.

Coal and residual oil (#6) have mineral ash content higher than distillate oil, natural gas, or wood and other vegetative fuels, and they produce higher PM emissions. PC boilers produce PM emissions composed almost entirely of inorganic material.

Boilers and other liquid and solid fuel combustors also emit uncombusted, carbonaceous  $PM_{10}$ , including droplets of liquid fuels, and these emissions also appear as smoke. When combustion efficiency is lower, such as in boilers with stoker and grate coal feed systems, or when oil and solid fuel boilers are not operating at capacity, significant amounts of unburned carbon PM are emitted. Emissions particles from coal and residual oil can stick to and coat boiler combustion chamber walls, reducing emissions, and the sulfur content of oil is correlated with PM from that fuel. When firing a low ash fuel, such as #2 distillate oil,  $PM_{10}$  and  $PM_{2.5}$  emissions are generally lower than from solid fuels. Gaseous fuels, like natural gas, have virtually no ash and burn completely, and therefore have no direct, primary  $PM_{10}$  emissions. A summary of  $PM_{10}$  EFs is presented in Table 3.6.

A comparison of the emission rates in Table 3.6 shows that coal ash content and burner configuration affect the PM emission rate of coal burning boilers. Also, diesel fuel engines emit more PM than engines using petrol.

The inorganic metal content of coals, including arsenic, chromium, lead, manganese, nickel, mercury, and radionuclides, varies depending on the coal seam. After combustion, most of these metals and other elements, such as radon, can be found in the ash. The metals may be carried up the boiler stack in the exhaust as fly ash PM<sub>10</sub> or as a condensable vapor, but they may concentrate in the heavier bottom ash. Elements in coal evenly distributed between fly and bottom ash typically include manganese, beryllium, cobalt, and chromium. Fly ash contains enriched elements such

<sup>&</sup>lt;sup>23</sup>Center for Climate and Energy Solutions, What is Black Carbon, April 2010, http://www.c2es.org/publications/black-carbon-climate-change, (accessed November 2016).

<sup>&</sup>lt;sup>24</sup>US EPA Office of Air Quality Planning and Standards, Prescribed Burning Background Document, EPA 450/2-92-003, 10, Research Triangle Park, 1992, https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=00001X20.PDF.

Table 3.6. Selected PM<sub>10</sub> emission factors

Source emission				Fuel
process	$PM_{10}$		Formula	content
Fireplace (dry wood) <sup>25</sup>	17.30	kg/Mg		
Bituminous cyclone boiler <sup>26</sup>	9.1	kg/Mg	$2.6 \times A$	7% ash
	15.6	kg/Mg	$2.6 \times A$	12% ash
Bituminous (PC, dry bottom) boiler <sup>27</sup>	8.05	kg/Mg	2.3 × A	7% ash
#6 (Residual) Oil Boiler <sup>28</sup>	1.67	kg/1,000 liters	$9.19 \times S + 3.22$	1% S
#2 Distillate oil boiler/furnace	1.67	kg/1,000 liters		
Natural gas boiler <sup>29</sup>	121.60	kg/Mm <sup>3</sup>		
Diesel fuel engine <sup>30</sup>	0.13	$\mu g/J$		
Petrol engine <sup>31</sup>	0.04	$\mu g/J$		
Clay crusher, grinder (dry) for bricks <sup>32</sup>	0.27	kg/Mg bricks		
Brick kiln <sup>33</sup>	0.68	kg/Mg bricks		
Paint manufacturing <sup>34</sup>	10.00	kg/Mg pigment		

 $\mu g/J$ : micrograms per joule

<sup>&</sup>lt;sup>25</sup>US EPA, AP-42 Chapter 1.9, Residential Fireplaces, 10/96, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s09.pdf, (accessed January 14, 2017).

<sup>&</sup>lt;sup>26</sup>US EPA, AP-42 Chapter 1.1 Bituminous and SubBituminous Coal Combustion, 9/98, page 1.1-1, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s01.pdf.

<sup>&</sup>lt;sup>27</sup>US EPA, AP-42 Chapter 1.1 Bituminous and SubBituminous Coal Combustion, 9/98, page 1.1-1, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s01.pdf.

<sup>&</sup>lt;sup>28</sup>US EPA, AP-42 Chapter 1.3, Fuel Oil Combustion, 5/10, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s03.pdf, (accessed January 14, 2017).

<sup>&</sup>lt;sup>29</sup>US EPA, AP-42 Chapter 1.4, Natural Gas Combustion, 5/10, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s04.pdf, (accessed January 14, 2017).

as arsenic, cadmium, lead, and antimony.<sup>35</sup> In 2005, U.S. EGUs using coal contributed more than half of the total U.S. anthropogenic PM emissions, and more than 25 percent of various metal emissions.

Trace elemental metals are also emitted from the combustion of oil. As with coal, the emission rate of metals in the PM is related to the metal content of the oil. Oil refining concentrates most of the ash, metals, and high molecular weight organic compounds into the #6 residual oil at the bottom of the distillation column.

The production of metals from ores rich in iron, copper, silver, and other materials requires significant amounts of energy, in addition to the mechanical extraction and sizing processes that emit PM. Depending on the energy needs of the specific heating and refining processes, combustion PM<sub>10</sub> and PM<sub>2.5</sub> emissions from the processes, furnaces, and power house may be very high.

#### 3.3 POLLUTANT EMISSIONS FROM OXIDATION

In addition to releasing trace un-combusted fuel and minerals as PM emissions, combustion *oxidizes* fuel constituents to generate CO<sub>2</sub> and the criteria pollutant gases CO, SO<sub>2</sub>, and NO<sub>2</sub>. Oxidized sulfur and nitrogen emissions are discussed in more detail in Section 3.3.2.

The chemical oxidation reaction also occurs in the human body and other life on earth, but without a flame. Known as *respiration*, it provides energy for organ function and energy for building living tissue, by splitting carbohydrate and fat molecules to release energy. The energy released also enables animals with circulation systems to transport oxygen and nutrients to the cells and remove the cellular oxidation byproduct,  $CO_2$ , which is then emitted. Plants and decomposition microorganisms also oxidize food and generate and "emit" the byproduct  $CO_2$ .

<sup>&</sup>lt;sup>30</sup>US EPA, AP-42 Chapter 3.3, Gasoline and Diesel Industrial Engines, 10/96, https://www3.epa.gov/ttn/chief/ap42/ch03/final/c03s03.pdf, (accessed May 12, 2017).

<sup>31</sup> Ibid.

<sup>&</sup>lt;sup>32</sup>US EPA, AP-42 Chapter 11.3 Brick and Structural Clay Product Manufacturing, 8/97, https://www3.epa.gov/ttn/chief/ap42/ch11/final/c11s03.pdf.

<sup>&</sup>lt;sup>33</sup>US EPA, AP-42 Chapter 11.3 Brick and Structural Clay Product Manufacturing, 8/97, https://www3.epa.gov/ttn/chief/ap42/ch11/final/c11s03.pdf.

<sup>&</sup>lt;sup>34</sup>US EPA, AP-42 Chapter 6.4, Paint and Varnish, 5/83, https://www3.epa.gov/ttn/chief/ap42/ch06/final/c06s04.pdf.

<sup>&</sup>lt;sup>35</sup>US EPA, Office of Air Quality Planning and Standards, *Locating and Estimating Air emissions from Sources of Arsenic and Arsenic Compounds*, EPA-454/R-98-013, June 1998, https://www3.epa.gov/ttnchie1/le/arsenic.pdf, (accessed July 7, 2017). Also AP-42 1.1 Bituminous Coal.

However, biota can release energy from carbon-based and other foods through an alternate process, chemical *reduction*. Under *anaerobic* conditions, sealed off from the atmosphere with little or no access to oxygen, biota digest organic compounds and waste by chemically reducing carbon and sulfur constituents for energy. The primary byproduct gases of anaerobic digestion or decomposition include methane (CH<sub>4</sub>) and TRS (total reduced sulfur compounds). CH<sub>4</sub>, the simplest carbon compound, is produced by many anaerobic biological systems and is also found in large quantities in fossil carbon deposits, extracted via wells, and sold as natural gas. These reduced gases can themselves be oxidized to CO<sub>2</sub> and SO<sub>2</sub>.

## 3.3.1 OXIDIZED CARBON EMISSIONS - CO<sub>2</sub> AND CO

 $\mathrm{CO}_2$  is colorless and odorless, and it mixes and circulates easily in the atmosphere at the concentration normally found in the modern atmosphere, 300 to 400 ppmv. It does not have a direct, toxic human health effect, and in water, it makes a slightly acidic solution.  $\mathrm{CO}_2$  has a molecular weight of 44 and is heavier than the  $\mathrm{O}_2$  and  $\mathrm{N}_2$  in the general atmosphere. The  $\mathrm{CO}_2$  emission rate from burning carbon fuels is usually more than two orders of magnitude higher than the criteria pollutant emission rates.

When only one oxygen atom is combined with a carbon atom from the fuel, CO is created. CO has a molecular weight of 28. If there is sufficient oxygen, time, and temperature, this odorless, colorless, criteria pollutant will oxidize further, adding a second oxygen atom to complete a  $CO_2$  molecule. CO forms a weak acid when combined with water.

An open fire or fireplace emits low amounts of CO and the other criteria pollutants. Coal and wood cook stoves change the combustion oxidation conditions and generally raise the emission rates. In boilers, furnaces, and engines, three factors significantly affect criteria pollutant generation and emission rates—the fuel, the feed systems for fuel and combustion air, and combustion chamber design.

Fuel combustion in a chamber offers advantages over open burning in the ambient atmosphere. Chambers and fuel feed systems designed for combustion better assure that the carbon or other material in the fuel is completely burned and energy recovered under the best conditions. Time, temperature, and turbulence, the three "Ts," are critical to how well a fuel burns and its energy can be used.

Temperature is key to combustion, and temperatures must remain above chemical ignition levels for enough time to burn all the fuel and maintain stable combustion conditions. The elevated temperature of the flame and combustion chamber causes constituent components of solid and liquid fuels to volatilize. These volatile organic carbon chemicals then ignite and combust. Combustion air must be heated to the same level, and because of this, a cooler air supply can lower combustion temperature and efficiency significantly.

Turbulence mixes the combustion air completely throughout the space where oxidation is occurring. The oxygen needed must be mixed into the burn zone thoroughly to reach all the fuel gas molecules without creating low-temperature areas.

Specific fuels and combustion conditions produce different emission rates for the same pollutant. Better combustion conditions occur when the flame is hotter, more fuel surface area can be heated evenly, and when oxidation can occur without obstacles. Several key features of the combustion process determine the concentration and amount of emissions:

- a. Fuel composition
- b. Fuel feed system or burner types for fuel types
- c. Design of the burning chamber and energy/heat transfer
- d. Capacity of the combustion equipment

CO<sub>2</sub> is directly related to the fuel composition and elemental carbon content. Fossil fuels and vegetation usually contain hydrogen as well as carbon, which when oxidized is emitted as *water* (H<sub>2</sub>O). However, H<sub>2</sub>O is often present as fuel moisture, and because it cannot oxidize further, it consumes energy from the combustion process as it changes phase from liquid to gas.

CO is also formed from the carbon in the fuel, but the emission rate of CO depends on the combustion efficiency.<sup>36</sup> It increases significantly if sufficient oxygen is not available to complete the oxidation reaction. Pelletized, dry, wood fuel burns with lower CO emission rates than logs and split wood. CO emission rates tend to be lower if the fuel oxidation *residence time* in the combustion chamber is longer. Lower efficiency can also result from smaller capacity designs, combustion chamber cooling due to high fuel moisture or low air supply temperature, and incomplete fuel and air mixing.<sup>37</sup> Engines, which have small combustion chambers and combust fuels for very short periods, produce more CO than boilers for the same heat input.

The variation in carbon content of coal, oil, and other fuels creates different  $CO_2$  emission rates. The CO EF is the same for all the PC boiler designs and is much lower than the rate for stoker boilers. The same CO EF applies to multiple oil combustor designs, but the natural gas EFs differ by size and burner configuration. (See Table 3.7.)

<sup>&</sup>lt;sup>36</sup>US EPA, AP-42 Chapter 1.3, Fuel Oil Combustion, 5/10, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s03.pdf, (accessed January 14, 2017).

<sup>&</sup>lt;sup>37</sup>Smaller combustors generally have a higher ratio of heat transfer surface area to flame volume than larger ones.

Table 3.7 CO<sub>2</sub> and CO emission factors

Source emission process	CO <sub>2</sub> (Mg)	CO (kg)	<b>Fuel Use Units</b>
Fireplace (wood)	1700	126.3	per Mg wood
Anthracite stoker boiler <sup>38</sup>	2840	0.25	per Mg coal
Bituminous stoker boiler	3020	5.0	per Mg coal
Bituminous (PC, dry bottom) boiler	3020	0.25	per Mg coal
#6 (Residual) oil boiler	3000	0.6	per 1,000 liter
#2 Distillate oil boiler/furnace	2676	0.6	per 1,000 liter
Propane combustor	1500	0.9	per 1,000 liter
Natural gas boiler	1920000	1344	per million m <sup>3</sup>
Natural gas tangential boiler	1920000	384	per million m <sup>3</sup>
Natural gas – residential furnace	1920000	640	per million m <sup>3</sup>
Brick kiln – coal fired	150	0.4	per ton brick
Brick kiln – natural gas fired	200	0.6	per ton brick
Plywood (softwood heating) <sup>39</sup>	45	1.45	per 93 m <sup>2</sup>

## 3.3.2 OTHER OXIDIZED CRITERIA POLLUTANTS - SO<sub>2</sub> AND NO<sub>2</sub>

Most commercial solid and liquid fuels contain *sulfur* and *nitrogen*, which are present in HC and other organic fuels from cell proteins. Elemental sulfur and nitrogen can oxidize to create  $SO_2$  and  $NO_2$ , which are gaseous criteria pollutants.  $SO_2$  emissions are directly related to the fuel sulfur content, while the  $NO_2$  emission rate is influenced both by fuel nitrogen content and other factors as well. These two criteria pollutants can combine with additional oxygen atoms in the atmosphere and become solid sulfate and nitrate compounds,  $PM < 1 \ \mu m$ .

Each coal seam, oil field, waste or wood fuel type has a different proportion of sulfur and nitrogen. Coal and residual oil (#6) have ash, sulfur,

<sup>&</sup>lt;sup>38</sup>US EPA, AP-42 Chapter 1.2, Anthracite Coal Combustion, 10/96, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s02.pdf, (accessed January 14, 2017).

<sup>&</sup>lt;sup>39</sup>US EPA, AP-42 Chapter 10.5, Plywood Manufacturing, 1/02, https://www3.epa.gov/ttn/chief/ap42/ch10/final/c10s05.pdf.

and nitrogen content higher than the other fossil fuels, distillate oil and natural gas, and they have higher PM emissions. The ash content of coal and oil<sup>40</sup> is also higher than that of wood and other vegetative fuels. PC boilers produce PM emissions composed almost entirely of inorganic ash materials. #2 distillate oil has very low ash content and its commercial sale in many areas is limited to oil with 0.3 percent or lower sulfur content. A more complete description of PM is in Section 3.2.

The SO<sub>2</sub> emission rates for combustion are directly related to the sulfur content of the fuel. However, under combustion conditions or processes that further oxidize the compound to SO<sub>4</sub>, SO<sub>2</sub> emissions can decrease slightly. Table 3.8. presents sample SO<sub>2</sub> EFs. SO<sub>4</sub> can be collected in ash or emitted as PM<sub>2.5</sub>. Water easily combines with or scavenges these

**Table 3.8.** Selected SO<sub>2</sub> emission factors

Emission source	Emission factor	EF formula	Sulfur content
Fireplace (dry wood)	0.4 kg/Mg wood		< 0.1%
Anthracite stoker boiler	13.65 kg/Mg coal	39 S/Mg	0.7% (0.8%)
Bituminous PC boiler	45.7 kg/Mg coal	38 S/Mg	2.4% (median)
	76.0 kg/Mg coal	38 S/Mg	4% (maximum)
#6 oil-fired boiler	18.8 kg/1,000 liters oil	157 S/1,000 gal	1.0%
#2 oil-fired boiler	5.1 kg/1,000 liters oil	142 S/1,000 gal	0.3% (median)
	8.5 kg/1,000 liters oil	142 S/1,000 gal	0.5% (maximum)
Natural gas boiler	9.6 kg/million m <sup>3</sup> gas		trace
Brick kiln (coal fired)	0.6 lb /1,000 Mg bricks		unspecified

<sup>&</sup>lt;sup>40</sup>US EPA, AP-42 Chapter 1.3, Fuel Oil Combustion, May 2010, page 1.3-2, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s03.pdf, (accessed January 14, 2017).

emissions and becomes acidic. SO<sub>2</sub> and exhaust moisture create corrosive conditions in a boiler or boiler stack.

As presented in Chapter 2, Table 2.2, bituminous coals may contain as much as 4 percent sulfur, and the sulfur content of anthracite and subbituminous coals is in the 1 percent range. Petroleum contains sulfur constituents, but most heavy oil, heating and diesel oil, and gasoline products from refineries are desulfurized. This is usually necessary to produce liquid fuels that meet market limits, generally under 1 percent in the U.S. commercial markets. High sulfur oils and gas are called "sour." Even though commercial natural gas has a low sulfur content, <sup>41</sup> small quantities of odorous sulfur compounds are added in transmission pipelines to alert people to leaks from the distribution lines or piping in a home or business. Wood contains less than 0.1 percent sulfur.

 $NO_x$  emissions are generated by two different chemical reactions. First, combustion converts a portion of the nitrogen in the fuel to nitrogen oxide (NO), a gaseous byproduct. The oxidation reaction continues, and this produces the more stable pollutant,  $NO_2$ , with a molecular weight of 46. The nitrogen compound emissions are molecules with either one or two oxygen atoms and together they are called *nitrogen oxides* ( $NO_x$ ). In a plume,  $NO_x$  appears slightly yellowish. Combined with moisture, it creates slight acidity. It also reacts with organic gas compounds in the atmosphere photochemically when temperatures are  $30^{\circ}\text{C}$  or higher.

The nitrogen content of coal and oil fossil fuels is generally higher than other fuels. Bituminous coal has the highest nitrogen content, which ranges from 0.5 to 2.0 percent.

Thermal oxidation also generates NO and  $NO_2$  from the  $N_2$  in the air supply if pressure or temperature is elevated from ambient conditions. Hotter combustion temperatures and efficiency can increase  $NO_x$  generation significantly, depending on how a) fuel supply and b) ignition create combustion conditions that satisfy the three Ts.<sup>42</sup> Under open, ambient pressure combustion conditions, thermal NO generation is rare because only a conflagration is hot enough and has enough energy to oxidize the atmospheric  $N_2$ .

As humans developed boilers and other combustion devices, fuel was fed into the fire manually, either by placing wood in a stove or shoveling chunks of coal into steam locomotive and boiler fireboxes. Mechanical feed systems for stoker boilers were developed that load or ram coal into

<sup>&</sup>lt;sup>41</sup>US EPA, AP-42 Chapter 5.3, Natural Gas Processing, 1/95, https://www3.epa.gov/ttn/chief/ap42/ch05/index.html.

<sup>&</sup>lt;sup>42</sup>https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s01.pdf. US EPA, AP-42 Chapter 1.1 Bituminous and SubBituminous Coal Combustion, 9/98, page 1.1-1, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s01.pdf.

the combustion chamber to burn in a layer on a grate. In contrast, coal used in the largest boilers at modern steam electric utility stations is pulverized and injected to the more completely sealed combustion chamber as small airborne particles (< 200 mesh sieve). This pulverized coal (PC) fuel preparation and firing configuration rate exposes more fuel surface area to oxygen and allows for more consistent, and higher, heat during combustion. Liquid and gas fuels are piped to a combustor and ignited in burners that are designed to maintain stable flame, consistent temperatures, and steady fuel feed to the combustion chamber.

 $NO_x$  formation increases in a boiler when flame and combustion chamber temperature is higher, oxygen concentration is higher, and the fuel oxidation *residence time* in the combustion chamber is longer. Decreasing any of these, or the steam output of a boiler, can reduce temperature and  $NO_2$  emission rates. The wide variety of combustion chamber design parameters are reflected in the many different  $NO_2$  EFs. Boilers with tangential (corner) firing burners emit less  $NO_2$  than those with burners configured horizontally across in the combustion chamber. AP-42 and other references describe the empirical relationships in more detail.

Reciprocating internal combustion engines burn fuels at high temperature under much higher pressure than boilers or other external combustion units, and emit  $\mathrm{NO}_2$  at a higher rate. Inside the combustion cylinders of a reciprocating internal combustion (IC) engine, the fuel burns explosively and moves a piston up and down. This rotates a crank that drives gears to turn wheels or a generator motor.

In conventional reciprocating engines, the ratio of the air supply to fuel is related to the emission rates, and higher air ratios, called "lean burn," reduce NO emissions. Diesel-fueled engines ignite at the temperatures produced by compressing the air and fuel injected into the cylinder. Petrol- or methane gas-fueled engines need a spark to ignite the fuel after it is injected into the cylinders. A Newer, gas-fueled, reciprocating IC engine designs achieve very lean, low NO<sub>x</sub> combustion with combustion prechambers and sophisticated, computer-controlled, monitoring and control of pressure, temperature, and fuel injection.

Gas-fired turbine engines convert energy from the gas flow and pressure of a combustion chamber exhaust into rotary motion. A sample of EFs is presented in Table 3.9.

<sup>&</sup>lt;sup>43</sup>C.R. Nave, Hyperphysics: Thermodynamics, The Diesel Engine, http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/diesel.html.Georgia State University. http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/diesel.html. Petrol/gasoline IC engines are designed with the Otto Cycle. Diesel engines use a design by Rudolph Diesel, who patented the cycle in the 1890s.

Table 3.9. Selected NO<sub>2</sub> emission factors

Source emission process	<b>Emission Factors</b>
Fireplace (dry wood)	1.3 kg/Mg
Bituminous (PC, wet bottom) boiler	15.5 kg/Mg
#6 (Residual) oil boiler – normal firing	5.64 kg/1,000 liters
#6 oil boiler – tangential firing	3.84 kg/1,000 liters
#6 oil boiler – commercial capacity	6.60 kg/1,000 liters
#2 distillate oil boiler/furnace	10.91 kg/1,000 liters
#2 oil residential heating furnace	2.16 kg/1,000 liters
Propane burner	1.56 kg/1,000 liters
Natural gas boiler (Large)	4480 kg/million m <sup>3</sup>
Natural gas boiler – tangential firing	2720 kg/million m <sup>3</sup>
Natural gas boiler/furnace (small)	1600 kg/million m <sup>3</sup>
Residential furnace	1504 kg/million m <sup>3</sup>
Gas turbine <sup>44</sup>	5000 kg/million m <sup>3</sup>
Brick kiln – coal fired	0.255 kg/Mg bricks
Brick kiln – natural gas fired	0.175 kg/Mg bricks
Brick kiln – sawdust fired	0.185 kg/Mg bricks

For the broad range of energy conversion processes, normalizing EFs to the activity measure of *heat input* provides a better perspective of how clean designs and process types are relative to one another.<sup>45</sup> Comparisons are shown in Table 3.10.

Nearly all NO<sub>2</sub>, SO<sub>2</sub>, CO, and CO<sub>2</sub> emissions from industrial sources are generated by the energy processes required for the production or manufacturing operations.

<sup>&</sup>lt;sup>44</sup>US EPA, AP-42 Chapter 3.1, Stationary Gas Turbines, 4/00, https://www3.epa.gov/ttn/chief/ap42/ch03/final/c03s01.pdf.

<sup>&</sup>lt;sup>45</sup>US EPA, AP-42 Appendix A: Conversion Factors for Various Substances, A-32, 9/85, https://www3.epa.gov/ttn/chief/ap42/appendix/appa.pdf.

Table 3.10. Energy emission factors based on heat input

Course process	DM	CO	CO	80	NO	VOC
Source process	PM	CO <sub>2</sub>	CO	SO <sub>2</sub>	NO <sub>2</sub>	VUC
	g/MJ	g/MJ	g/MJ	g/MJ	g/MJ	g/MJ
Fireplace (dry wood)	0.93	91.36	6.77	0.01	0.07	6.15
Anthracite stoker boiler	0.01	98.28	0.01	0.42	0.00	0.00
Bituminous stoker boiler	0.24	88.41	0.09	2.72	0.00	0.00
Bituminous (PC, dry bottom) boiler	0.12	88.41	0.01	2.72	0.39	0.00
#6 (Residual) oil boiler	39.93	71.18	14.35	450.64	134.90	0.80
#6 oil boiler – tangential firing	39.93	71.18	14.35	450.64	91.85	0.80
#2 distillate oil boiler/furnace	10.30	70.10	15.60	221.51	62.40	0.62
Residential heating-#2 oil	5.30	70.10	15.60	221.51	56.16	2.22
Propane	3.42	58.25	36.66	0.08	63.54	3.91
Natural gas boiler	12.38	50.29	35.06	0.25	116.87	2.30
Natural gas residential furnace	12.38	50.29	16.70	0.25	39.24	2.30

# 3.4 SECONDARY PM, LEAD, AND OTHER METAL EMISSIONS

Combustion exhaust contains some byproduct compounds created during high temperature oxidation that condense into tiny, spherical  $PM_{2.5}$  particles as the hot exhaust stream cools. Studies show that approximately 10 percent of the total  $PM_{10}$  emissions from oil are secondary  $PM_{2.5}$  emitted from a stack as a gas, but which convert to PM in the ambient air.

Emissions may continue to oxidize or react into secondary solid compounds. Fuel sulfur will be emitted as SO<sub>2</sub>, but over time in the atmosphere, emissions can convert to a solid PM<sub>2.5</sub> compound, sulfate, SO<sub>4</sub>. This conversion has been found to be sufficiently common that

stricter SO<sub>2</sub> control is now required in many air districts or regions to achieve PM<sub>2.5</sub> air quality standards.

The metal lead, Pb, the sixth criteria pollutant, is the only pollutant added to the list of criteria pollutants (1976) after the CAA was passed. Car manufacturers had worked with refineries to produce petrol (gasoline) with lead additives, so that engines would operate with less knocking. As this leaded fuel was burned in cars, lawnmowers, and other engine-driven machines, the lead compounds were emitted as  $PM_{2.5}$  from the tailpipes.

Initially, the approach to reducing Pb emissions was believed to be a simple ban on using these additives in automobile fuel. However, the Pb emissions from the millions of mobile sources, ore smelters, and battery manufacturers placed an enormous burden on the environment and created widespread, elevated ambient concentrations. In 1976, in the Boston area alone, with a population between 2 and 3 million people, stormwater washed approximately 200 Mg of Pb from the vehicle emissions to the wastewater treatment plants each year. <sup>46</sup> A court suit directed EPA to list it as a criteria pollutant, and it was put on the list in 1976. <sup>47</sup>

Metals are found in fuel emission compounds, as constituents of the primary  $PM_{10}$ , as secondary condensable  $PM_{2.5}$ , or as gases. Information on metal content in coal was presented in Section 3.2.2. The metal mercury, Hg, is a gas emission because it can be a vapor at normal ambient temperatures. After more sensitive Hg emission monitoring methods were developed, it was detected as an emission from burning coal and other fossil fuels and found to be a significant portion of the remaining Hg emission inventory. The EPA required large, coal-fired electric plants to install capture systems to reduce emissions of this HAP. Small amounts of Hg are also emitted from oil, natural gas, and wood bark combustion.

Coal and oil contain the element chlorine from salt in and around the fossilized plant cells it was made from, and combustion of these fuels emits the HAP, hydrogen chloride (HCl). AP-42 indicates that some of the chlorine remains in the ash, but the mean HCl emission rate is 0.6 kg/Mg. Industrial sources of direct HCl emissions are chlorine chemical production and chlorinated organic chemical manufacturing, including some plastics. Equipment burning any gas with chlorine content, including thermal systems to control evaporative emissions from organic dry cleaning and other solvents, will produce HCl emissions.

Addition of Lead to List of Air Pollutants, FR Doc76-10157, Notices, March 31, 1976, https://www3.epa.gov/ttn/naaqs/standards/pb/data/PB\_listing\_1976%20FR.pdf.

# 3.5 ORGANIC COMPOUND (OC) EMISSIONS FROM ENERGY AND INDUSTRY

VOC emissions are primarily aliphatic, oxygenated, and relatively low molecular weight aromatic compounds which exist in the vapor phase at ambient temperatures. HC compounds as large as  $C_6H_{14}$  (hexane)<sup>48</sup> and other VOC comprise over 90 percent of the OC emissions. VOC includes esters, phenols, and polycyclic organic matter (POM<sup>49</sup>). OC chemical species are not considered to be VOC if they do not participate in the ozone/photochemical reactions. This excludes compounds such as methylene chloride, methane, and chlorinated or fluorinated organics (HCFC) such as chlorodifluoromethane, best known under its trade name Freon<sup>TM</sup> or CFC-22.

Due to the different molecular weights of the many OC in combustion or process emissions, volumetric concentrations of individual OC species measured in an exhaust stream or in the air cannot be added together directly to get a total concentration for calculating OC emissions. Concentrations must be converted to a single equivalent chemical, for example methane or propane, to determine a molecular weight for calculating mass emission rates accurately. Some monitors are capable of measuring the total organics with a chosen equivalent like methane. Sensitive equipment that can analyze gaseous OC pollutants in air samples can provide results in the parts per million by volume (ppmv) or parts per billion by volume (ppbv) units.

## 3.5.1 VOC AND HAP OC EMISSIONS FROM ENERGY PROCESSES

Small amounts of un-combusted, organic fuel compounds are emitted during energy generation. Unburned HC emissions comprise most vapor phase, OC emitted from a combustion source, and emission rates vary with the type of fuel and firing configuration. VOC emissions are highest during periods of incomplete combustion or low-temperature combustion, such as the start-up or shut-down cycle for oil-fired boilers.

AP-42 indicates the VOC emissions from oil combustion include alkanes (simple carbon bonds), alkenes, aldehydes, and carboxylic acids, as well as substituted benzenes and some other carbon ring compounds (e. g., benzene, toluene, xylene, and ethyl benzene), 50 which are HAPs.

<sup>&</sup>lt;sup>48</sup>J Rank Science & Philosophy, Science Encyclopedia website, Hydrocarbons – Carbon's Chemical Bonding, Hydrocarbon-Alkanes page, http://science.jrank.org/pages/3437/Hydrocarbon-Alkanes.html.

<sup>&</sup>lt;sup>49</sup>A related group of similar chemicals is called polycyclic aromatic hydrocarbons (PAH). PAH monitoring information was used in some of the early photochemical studies.

<sup>&</sup>lt;sup>50</sup>US EPA, AP-42 Chapter 1.3, Fuel Oil Combustion, 5/10, https://www3.epa.gov/ttn/chief/ap42/ch01/final/c01s03.pdf, (accessed May 12, 2017).

Emissions of the HAPs benzene, toluene, ethylbenzene, and xylene, often known by the abbreviation "BTEX," are significant because petrol contains significant amounts of these OC. Combustion destroys organic constituents of the fossil fuels, coal, oil, petrol, and natural gas, and it reduces the OC emission rate to only a fraction of the fuel content. With efficient combustion, the VOC and OC HAP fuel constituent emission rates are an order of magnitude, or more, lower than the fuel content.

Combustion equipment testing shows that fossil fuel combustion equipment also emits formaldehyde (CH<sub>2</sub>O),<sup>51</sup> an organic chemical on the HAP list. It is not present in fuels. CH<sub>2</sub>O is an intermediate product generated during OC oxidation and reduction chemical reactions, and it participates in some reaction pathways yielding CO. Elevated CH<sub>2</sub>O concentrations occur in the atmosphere during smog conditions because it is generated and then consumed during photochemical oxidation and other reactions—no direct anthropogenic emissions are required. It is not well understood exactly how combustion generates CH<sub>2</sub>O emissions, but the AP-42 Fuel Oil Combustion section (AP-42 Chapter 1.3, 2010) provides the theory that although it is formed during combustion, it is also destroyed in high temperature and efficient and stable combustion.

Processes to prepare commercial natural gas remove oxygen and  $\mathrm{CO}_2$  from the methane and other trace, combustible, organic gases before the product is distributed and sold to customers. In addition to the emissions generated from processing natural gas, leaks from compressors and piping connections emit methane ( $\mathrm{CH}_4$ ) and other HC during the transmission of liquid and fossil fuels to market or during storage. Similar VOC emissions may come from container leaks or engine energy production when the fuel is transported in vehicles.

#### 3.5.2 VOC AND HAP OC EMISSIONS FROM INDUSTRY

The petrochemical industry processes, from the oil or gas field to the end user, emit significant amounts of VOC emissions. Thermal or catalytic cracking processes produce fuel and feedstock materials. The refinery processes known as *reforming* or *isomerization*<sup>52</sup> combine small, lighter molecular oil compounds into polymers and rearrange molecular structures. At each point in these processes, some of the feedstock, intermediate, and

<sup>&</sup>lt;sup>51</sup>US EPA, Locating and Estimating Air Emissions from Sources of Formaldehyde (Revised), EPA-450/4-91-12, March 1991, https://www3.epa.gov/ttn/chief/le/formal.pdf, (accessed May 12, 2017).

<sup>&</sup>lt;sup>52</sup>US EPA, AP-42, Chapter 5-1, Petroleum Refining, 4/15, https://www3.epa.gov/ttn/chief/ap42/ch05/final/c05s01\_2015.pdf, (accessed May 12, 2017).

product organic compounds can be lost to the atmosphere. The large amount of energy needed for crude oil distillation and cracking produces energy generation emissions. HC and VOC emissions are released from storage containers and tanks of the products that are highly volatile and evaporative.

The chemical industry develops and uses liquid and solid organic compound feedstocks to produce synthetic organic materials and plastics. In processing organic chemicals, basic light organic compounds, "monomers," are linked together into resins and other plastic molecules. The equipment and piping making each product and intermediate can leak.<sup>53</sup> For example, the synthetic chemical polyester is made from the monomer ethylene, liquid at ambient temperature, which can then be spun into synthetic fibers or molded into packaging. Some chemical manufacturers add inorganic compounds, e.g., ammonia and acids, to petroleum-based or carbon feedstocks to produce other materials. Inks and varnishes are cooked at temperatures up to 315°C, and the OC content boils off as emissions, if not captured. The factories making these products use considerable amounts of energy in these processes. The HAP CH<sub>2</sub>O can evaporate from processes using it as an input material, such as the chemical production of liquid CH<sub>2</sub>O or adhesives, or if glue containing formaldehyde is used in plywood or carpets.

Manufacturing and other processes that use organic feedstocks or that coat parts and structures emit VOC. Cement and ore production processes emit VOC as does the manufacture and installation of building materials and roadways. In the USEPA WEBFIRE database, the most common industrial VOC emission factors are for the chemical manufacturers that use or produce the HAPs BTEX in liquid or gaseous form.

Paint and other coating manufacturers disperse solid pigments into organic and water-based liquids to prepare them for application. Residential and manufacturing users must allow the liquid to evaporate before the coating remains to protect the surface.

Storage tanks are required not only for fuels and feedstocks but also for the volatile organic liquids and gases used for cleaning. The feedstock tanks, application and cleaning systems emit VOC if vapors are not contained. In addition, the vapors in the air space in the tanks are in equilibrium with the evaporation rate of the liquid. They are pushed out of the tank when it is refilled and will be emitted if special capture equipment is not used. Industry sectors that need extensive cleaning processes, including food, health-related devices and services, and electronics, emit

<sup>&</sup>lt;sup>53</sup>AAUS EPA,US EPA,US EPA,AP-42, Chapters 6.6-1 and 2: Introduction to Plastics, Polyvinyl Chloride and poly(ethylene terephthalate), 9/91, https://www3.epa.gov/ttn/chief/ap42/ch06/final/c06s06-1.pdf.

**Table 3.11.** VOC emission factors

Source emission process	EFs (with Units)
Fireplace (dry wood)	114.5 kg/Mg
Bituminous (PC, wet bottom) boiler	0.02  kg/Mg
#6 (Residual) oil boiler – normal firing	0.034 kg/1,000 liters
#2 distillate oil boiler/furnace	0.024 kg/1,000 liters
Residential heating oil furnace	0.09 kg/1,000 liters
Propane burner	0.10 kg/1,000 liters
Natural gas boiler (large)	88.0 kg/mm m <sup>3</sup>
Diesel fuel engine	$0.15~\mu g/J$
Gasoline engine	$1.30~\mu g/J$
Brick kiln – coal fired	0.01 kg/Mg bricks
Brick kiln – natural gas fired	0.01 kg/Mg bricks
Brick kiln – sawdust fired	0.09 kg/Mg bricks
Paint manufacturing	15 kg/Mg product
Plywood heater (softwood) <sup>54</sup>	0.5 kg/ 93 m <sup>2</sup> plywood

significant amounts of VOC unless they use only water-based cleaners. Table 3.11, includes some selected VOC EFs.

Finally, industrial processes that use or manage materials containing HAPs or input pure HAP materials generally have some quantity of HAP emissions. Although some are metals, many of the HAPs are OC, including pesticides and chlorinated OC. The EPA has published a series of Locating and Estimating reports (L&E) that review industrial emission sources of HAPs,<sup>55</sup> including acrylonitrile, BTX, carbon tetrachloride, dioxins, formaldehyde, perchloroethylene, polycyclic organic matter (POM), styrene, and others. A short discussion of HAP health effects can be found in Chapter 4, Section 4.4.4 with links to more detailed information.

<sup>&</sup>lt;sup>54</sup>US EPA, AP-42, Chapter 10-5, Plywood Manufacturing, 1/02, https://www3.epa.gov/ttn/chief/ap42/ch10/final/c10s05.pdf.

<sup>&</sup>lt;sup>55</sup>US EPA, Air Emission Factors and Quantification, Locating and Estimating Documents, https://www.epa.gov/air-emissions-factors-and-quantification/locating-and-estimating-le-documents, (accessed July 7, 2017).

Hg, benzene, and other OC HAP constituents of coal become emissions when raw coal is used to produce coke or when industries combust coal for power.

Hg was used in making felt hats a century ago and seeped into the fabric. Although most manufacturing eliminated the use of Hg in products and raw materials, it is still emitted as a trace ash constituent from coal combustion (approximately half the United States emission burden in 2005) and from a few other metal processing industries. Only a few tests in WEBFIRE show the presence of Hg emissions for industrial processes, notably those producing asphalt concrete, cement, and lime or those from iron, aluminum, and lead refining. The high temperatures required for metal smelting and heating, including zinc, can emit metals in gas form.

Mining uranium and phosphorus emits radon and radionuclides. Rocket fuel contains beryllium, which is emitted during rocket testing and firing, and arsenic is emitted from glass manufacturing, primary copper smelters and arsenic production facilities.

# 3.6 ESTIMATING EMISSIONS FROM OTHER SOURCES

Emissions of *area* sources, any group of numerous small emission sources or sources without a single stack vent, are estimated through fuel use data, area liquid sales information, or emission model calculations.

Home and small building heating emission calculations are based on fuel use totals and assumptions about equipment and EFs. Other area sources, like vehicle fueling stations, emit evaporated fuel vapors. Automobile service stations and other small businesses that machine or assemble parts generally use organic solvents for cleaning. The storage containers for these cleaners and degreasers are potential VOC emission sources. VOC emission inventories for these area source processes are estimated using EFs and the amount of VOC liquids used.

Mobile sources, car, truck, train, ship, and aircraft, originally had emission factors in AP-42 Volume II, but these have been replaced with emission simulation models. These can better account for the complex parameters contributing to the emissions of vehicles travelling on the roadways. Different engine sizes and types have different emission profiles, and emissions also differ by factors including vehicle speed, miles travelled, fuels, fuel and oil evaporation, temperature, and start-up conditions. The EPA Office of Transportation and Air Quality (OTAQ) originally developed separate emission models for roadway and nonroad

mobile sources, MOBILE, and NONROAD. These have been incorporated into the MOtor Vehicle Emission Simulator (MOVES) to determine more accurate criteria and toxic pollutant factors and emission calculations. <sup>56</sup>

Emission models can calculate emissions for sources without defined vents, including landfill decomposition gas (LandGEM version 3.2),<sup>57</sup> agriculture fertilizer, and biogenic emissions. Evaporative emission rates from TANKS<sup>58</sup> are also the result of multiple parameters and can be calculated more accurately with an emissions model.

Emission models can be used to calculate individual source emissions but often are used as data preparation tools that format emissions for input to complex, regional air quality models. Hourly, air quality predictions for regions large than 50 kilometers require massive amounts of data, and emission databases, like the EPA SPECIATE, <sup>59</sup> provide input with details on hourly emissions of individual VOC compounds as well as size distributions and composition of PM. Modeling to simulate dispersion and air quality conditions is presented in Chapter 6.

<sup>&</sup>lt;sup>56</sup>US EPA Office of Transportation and Air Quality, MOVES webpage, https://www.epa.gov/moves has information on mobile source emission factors and training to use the model.
<sup>57</sup>US EPA Clean Air Technology Center, Software Products, https://www.epa.gov/catc/clean-air-technology-center-products#software.

<sup>&</sup>lt;sup>58</sup>US EPA, Air Emissions Modeling, https://www.epa.gov/air-emissions-factors-and-quantification/emissions-estimation-tools.

<sup>&</sup>lt;sup>59</sup>US EPA, Air Emissions Modeling, SPECIATE [VOC emissions], https://www.epa.gov/air-emissions-modeling/speciate-version-45-through-40. Also linked to https://www.epa.gov/air-emissions-factors-and-quantification/emissions-estimation-tools.

## DIRTY AIR AND ITS EFFECTS

### 4.1 FIRST AIR QUALITY ISSUES

Air contaminants released from natural earth systems and human activities can harm people's health as well as the world they live in, their *welfare*. A typical air pollution regulation broadly defines pollution as: contaminants in concentrations or duration that cause a nuisance; injure human, plant, or animal life or property; or which unreasonably interfere with the comfortable enjoyment of life, property or the conduct of business.<sup>1</sup>

Before the Industrial Revolution, contaminants naturally released by volcanos or made airborne by wind could be harmful to living creatures on the surface of the earth. For example, the sulfur compounds,  $H_2S$ , TRS, and  $SO_2$ , from volcanic eruptions are all poisonous, toxic emissions because they harm human health and create acidic atmospheric conditions that stress vegetation, harm animals and other biota, and increase the corrosion activity of rocks and soils. CO and hydrogen fluoride (HF) are also acidic.

In 1986, a natural explosion of  $CO_2$  that had built up under the bottom of Lake Nyos in West Cameroon<sup>2</sup> had lethal results, asphyxiating 1800 people as well as animals in settlements up to 25 km away. This situation, with all the oxygen displaced by the heavier  $CO_2$ , was not unique, even in the area affected. Smaller events like it had occurred in the same area and other nearby lakes only a decade before.

Human pollution sources can create nuisances and poor air quality—dusty roads, agriculture smoke from the use of peat and wood fuels, and agricultural burning. Royal decrees and bans were issued to combat coal smoke pollution in England and Germany as early as the

<sup>&</sup>lt;sup>1</sup>City of Boston (Massachusetts), Air Pollution in Boston, http://www.cityofboston.gov/environment/airpollution/, (accessed November 12, 2016).

<sup>&</sup>lt;sup>2</sup>Nyos Degassing Project. Disaster at Nyos, http://www.degassing-nyos.com/pages/overview.html, (accessed February 13, 17).

13th and 14th centuries.<sup>3</sup> Noisome businesses, like pig farm operations, have often polluted neighbors' living spaces with their notable air and water releases. However, as recently as 300 years ago, wind and changing weather could usually disperse contaminants to nondetectable concentrations, and precipitation could absorb and wash enough contaminants out of the air to achieve good air quality quickly again.

# 4.2 HUMAN IMPACT AND AIR POLLUTION EPISODES

By the 18th century, as people settled in larger towns and cities, heating and cooking emissions became more concentrated, and smoke polluted the air more frequently and for longer periods. There were good days with low PM concentrations, but indoors or out, tallow candles, stoves, locomotives, and industrial smokestacks all contributed to dirty air everyone was breathing.

London was one bustling center of industry with smoke often so thick that one side of the street would not be visible from the other. Sometimes the air would remain thick with smoke and fog for several days and records show that the smell of coal tar hung in the air. One record from 1813 noted that the heavy smoke and fog combined was particularly filthy and uncomfortable.<sup>4</sup> Smoke and SO<sub>2</sub> emissions in the cities and towns interacted with normal moisture in the air to create acid droplets, causing even worse effects than the PM alone. Certain periods of cold and damp days in the winter could bring especially high concentrations of smoke particulates to London.<sup>5</sup> Weather and ambient air conditions that trap emissions are discussed further in Chapter 6 in the discussion of the physics of the atmosphere.

As the Industrial Revolution evolved, homes and industry burned more and more coal, and poor air quality and billowing smoke became a hallmark of the period. Industrial growth expanded rapidly, producing byproducts,

<sup>&</sup>lt;sup>3</sup>C.I. Davidson. (1979). "Air Pollution In Pittsburgh: A Historical Perspective." *Journal of the Air Pollution Control Association*, 29, no. 10, pp. 1035-1041, doi:10.1080/00022470. 1979.10470892, http://www.tandfonline.com/doi/abs/10.1080/00022470.1979.10470892, (accessed November 12, 2016).

<sup>&</sup>lt;sup>4</sup>Royal Geographic Society. Met Office Education. "London's Killer Smog." http://www.rgs. org/OurWork/Schools/Teaching+resources/Weather+and+climate+resources/Key+Stage+Three/Londons+killer+smog.htm, (accessed May 11, 2017).

<sup>&</sup>lt;sup>5</sup>K.C. Heidorn, and Ontario Ministry of the Environment, Canada. "A Chronology of Important Events in the History of Air Pollution Meteorology to 1970." *Journal of the American Meteorological Society*, http://journals.ametsoc.org/doi/pdf/10.1175/1520-0477 1978)059%3C1589:A-COIEI%3E2.0.CO%3B2, (accessed June 8, 2017).

often emitted or wasted. Inefficient coal combustion in early boilers and stove generated clouds of black smoke. Smoke and soot were everywhere. Local transportation presented a nuisance, too, relying on horse power.

The welfare of homemakers was affected, with frequent cleaning necessary for soot deposits once or twice a day. Fortunately, the intense build-up of indoor air pollution from cooking, heating stoves, and the new fashion of tobacco smoking could be vented and added, a bit diluted, to the public air space. By the late 19th-century, the crusade to promote good health pure, nutritious food, clean water, and air had started. Scientists like Ellen H. Richards understood the impact of poor air quality well enough to encourage homemakers to throw open the windows to let fresh air in on low-smoke days.

The contribution of visible smoke PM to air pollution was understood and could be monitored from a smokestack with the Ringelmann scale. In 1880, an individual in St. Louis, Missouri, was awarded a \$50 fine for an "obnoxious nuisance" caused by smoke from a nearby chimney.<sup>6</sup>

A particularly deadly air quality episode in London in December 1873 was found to have produced a 40 percent increase in the death rate. Other bad episodes occurred in London in 1880, 1882, 1891, and 1892, with the 1892 episode resulting in more than 600 excess deaths. An episode of <a href="mailto:smook">smooke</a> and <a href="fog-was first called">fog-was first called</a> "smook" in a paper for the 1905 Public Health Congress.<sup>7</sup>

Episodes also occurred in many other industrial areas. Physical geography of a valley can trap emissions to some extent, and as described in Chapter 6, stagnant atmospheric conditions produce the worst air quality concentrations. A "poisonous fog" descended on Belgium's Meuse Valley, a center of steel production, in 1897. Again in 1930, another episode in the Meuse Valley resulted in more than 60 excess deaths, with serious health problems affecting an additional 6,000 people. In December 1948, the town of Donora, Pennsylvania, experienced a thick yellow blanket of smog that sickened more than 3,000 people and ultimately killed 20.8 The website for the episode describes how the metal, SO<sub>2</sub>, and other emissions

<sup>&</sup>lt;sup>6</sup>W. G. Christy, Consulting Engineer. (1960). "History of the Air Pollution Control Association." *Journal of the Air Pollution Control Association* 10, no. 2. http://www.tandfonline.com/doi/abs/10.1080/00022470.1960.10467911?tab=permissions&scroll=top.

<sup>&</sup>lt;sup>7</sup>K.C. Heidorn, and Ontario Ministry of the Environment, Canada. "A Chronology of Important Events In the History of Air Pollution Meteorology to 1970." *Journal of the American Meteorological Society*, http://journals.ametsoc.org/doi/pdf/10.1175/1520-0477 1978)059%3C1589:A-COIEI%3E2.0.CO%3B2, (accessed June 8, 2017). Dr. Henry Antoine DesVoeux (of London) coined the term smog for "Fog and Smoke" in a paper.

National Public Radio (NPR). All Things Considered, Smog Deaths In 1948 Led To Clean Air Laws, http://www.npr.org/templates/story/story.php?storyId=103359330, (accessed August 11, 2016).

from the local zinc smelter, steel mills, and railyards were trapped for a period of four days, concentrating in the valley at deadly concentrations.<sup>9</sup>

A four-day air pollution episode in London in 1952 is blamed for more than 4,000 deaths. <sup>10</sup> Observers wrote of "smoke pouring from the chimneys." During this 1952 London episode, emissions were estimated to have been approximately 1,000 Mg of smoke particles, with enough gaseous, acid-forming emissions to generate 800 Mg of sulfuric acid. It is likely that over 150,000 tons of coal were burned in London during the period. Weather conditions in the lowest layer of the atmosphere had trapped the pollutants and concocted a deadly stew.

In 1955, one of the people who brought attention to the need for a national air quality law in the United States was the famous radio star, Walter Winchell, making the case for public support during a broadcast. Two minor, federal clean air laws were passed in the United States before 1962, the year when London again experienced 750 deaths from a smog episode. The New York City area faced an episode over the 1966 Thanksgiving Day weekend that was the cause of 48 deaths in the city alone.

The tremendous toll of the 1952 London catastrophe was not repeated in Europe or North America again. Nonetheless, as late as the early 1970s, air flight plans were occasionally rerouted on a rare, clear night to show passengers the view of the bright, sparkling lights of Manhattan.<sup>12</sup>

The pungent smell of many catastrophic smog incidents led local, state, and federal researchers and university scientists to investigate the causes and health effects of emissions beyond PM. Pollution from the sulfur in coal had an acrid odor, but did not explain other examples of poor air quality. Knowing that high concentrations of both particles and sulfur dioxide caused significant health problems, engineers and researchers were looking for ways to control some pollutants at their source—ways to remove sulfur from fossil fuel, designs for more efficient boilers, burners, and engines and new, cleaner fuel types that would produce fewer emissions.

A notable smog episode in Los Angeles, in 1943, was traced back to a new, petrochemical plant emitting a visible orange cloud into the air basin, It was cracking petroleum to produce the synthetic organic compound

<sup>&</sup>lt;sup>9</sup>Donora Historical Society and Smog Museum. 1948 Smog, https://www.sites.google.com/site/donorahistoricalsociety/1948-smog, (accessed November 8, 2016).

<sup>&</sup>lt;sup>10</sup>Royal Geographic Society. Met Office Education, "London's Killer Smog," http://www.rgs. org/OurWork/Schools/Teaching+resources/Weather+and+climate+resources/Key+Stage+Three/Londons+killer+smog.htm, (accessed May 11, 2017).

<sup>&</sup>lt;sup>11</sup>History Channel. 1948, October 29, Killer smog claims elderly victims, http://www.history.com/this-day-in-history/killer-smog-claims-elderly-victims.

<sup>&</sup>lt;sup>12</sup>Interview with USEPA Region 1 Engineer, Thomas Doane, regarding a return flight to Boston from EPA headquarters in Washington, DC, circa 1971.

butadiene, an unsaturated HC. This new kind of smog, a mix of organic compounds, oxidants, and other pollutants, reduced visibility to three blocks and caused breathing problems and eye irritation for most people in the valley. <sup>13</sup> Researchers from the California Institute of Technology were able to measure this new kind of smog by the effect on spinach and alfalfa. <sup>14</sup> They were able to measure the total pollution level, the overall intensity, by how much it created cracks in exposed rubber tubing. The ability to quantify specific, ambient OC and oxidants, including O<sub>3</sub>, at lower concentrations in real-time would come several decades later.

On the trail of the largely invisible pollutants, California government agencies and others researched the role of car emissions and the amount of their emissions in the increasingly congested cities. Professor Arie Jan Haagen-Smit of the California Institute of Technology switched his research from the organic terpenes and hormones emitted by plants to air pollution HC and OC emissions in 1948. CO, an engine combustion emission, was already known to produce acute health effects when local carbon monoxide concentrations had become elevated. Dr. Haagen-Smit found that vehicle engine tailpipe emissions also had significant amounts of unburned hydrocarbons from petrol and diesel fuels. His research determined that the third predominant engine emission, NOx, was also a precursor, a major input chemical, of photochemical smogs.

Television station KCET has reporting and photographs of Los Angeles smog events<sup>16</sup> in 1943, 1948, and 1963. The City actually crowned a woman its "Smog Queen" in 1951 to draw attention to the problem. In keeping with the times, at least one person built a "smog alert chamber" underground to escape the dirty air. *Los Angeles Times* reported a particularly bad episode in September 1955<sup>17</sup> when delivery workers appeared on the streets with company-issued gas masks. By 1963, the U.S. Public Health Service was charged with supporting national research on

<sup>&</sup>lt;sup>13</sup>California Air Resources Board (CARB). Key Events in the History of Air Quality in California, http://www.arb.ca.gov/html/brochure/history.htm#1930, accessed A video tracking California air pollution and control programs at https://www.arb.ca.gov/videos/clskies.htm.

<sup>&</sup>lt;sup>14</sup>National Academy of Science, Arie Jan Haagen-Smit. 1900-1977, A Biographical Memoir, http://www.nasonline.org/publications/biographical-memoirs/memoir-pdfs/haagen-smitarie.pdf.

<sup>&</sup>lt;sup>15</sup>CARB, Arie Haagen-Smit, https://www.arb.ca.gov/html/haagen-smit.htm, (accessed October 9, 2016).

<sup>&</sup>lt;sup>16</sup>KCET, History, LA's Smoggy Past, in Photos, N. Masters, March 17, 2011, https://www.kcet.org/shows/lost-la/las-smoggy-past-in-photos, (accessed July 29, 2017).

<sup>&</sup>lt;sup>17</sup>Los Angeles Times, Photography, Framework, Fighting Smog with Gas Masks, September 14, 1955, http://framework.latimes.com/2014/08/26/fighting-smog-with-gas-masks/, (accessed June 29, 2017).

vehicle contaminant emissions, harmful concentrations, and methods to reduce emissions, as discussed in Chapter 5.

The United States and Europe no longer face the level of air pollution and the related health burden that existed in the mid-20th century, but in other parts of the world, especially those which are transitioning to industrial economies, episodes continue to occur frequently. The pollution problems in Shanghai and Beijing, China, were a significant concern for the athletes of the 2008 Summer Olympics, hosted in Beijing. China solved the problem in the short term by closing down coal-burning industries for the duration of the games and limiting car traffic (reducing emissions) in the city. Monitoring in China during a significant dust and haze event in late April 2012 indicated that PM2.5 concentrations were nearly three times the U.S. NAAQS. 18 In late January 2013, an episode affecting two-thirds of the country's major cities sent more than 7,000 children to the hospitals in Beijing alone. The 2015 China Air Quality Management Assessment Report by the Clean Air Alliance of China<sup>19</sup> reported that air quality is improving in most of China, but more than 170 air quality warnings were issued in 2014; 18 of them for Beijing. As frequently reported in the media, many Chinese in the megacities wear fine particulate respirator masks on hazy, poor air quality days.

Smog episodes are not the only way people are exposed to dangerous air quality. If equipment failures or fires occur at manufacturing plants producing or using hazardous materials, or if trucks and trains carrying them are accidentally damaged, the sudden releases to the air can be catastrophic. In December 1984, a Union Carbide (now Dow Chemical) plant in Bhopal, India, was manufacturing pesticides, when water seeped into a tank storing the HAP methyl isocyanate. The reaction that followed caused approximately 27 Mg of methyl isocyanate and other toxics to be forced out the relief valve.<sup>20</sup> The plume remained close to the ground, killed at least 6,000 people, and exposed more than 500,000 to the toxic gas with lasting effects.<sup>21</sup>

<sup>&</sup>lt;sup>18</sup>T. Yang, Y. Sun, W. Zhang, Z. Wang, and X. Wang. (2016). "Chemical Characterization of Submicron Particles during Typical Air Pollution Episodes in Spring over Beijing." *Atmospheric and Oceanic Science Letters* 9, no. 4, pp. 255-262. doi:10.1080/16742834.2016.1173509, published 21 May 2016, http://www.tandfonline.com/doi/abs/10.1080/16742834.2016.1173509, (accessed June 29, 2017).

<sup>&</sup>lt;sup>19</sup>Clean Air Alliance of China, 2014 Annual Report, http://en.cleanairchina.org/prod-uct/7055.html, (accessed July 7, 2017).

<sup>&</sup>lt;sup>20</sup>Union Carbide. Cause of the Bhopal Tragedy, http://www.bhopal.com/Cause-of-Bhopal-Tragedy, (accessed July 12, 2017).

<sup>&</sup>lt;sup>21</sup>A. Taylor. "Bhopal: The World's Worst Industrial Disaster, 20 Years Later." The Atlantic Magazine, https://www.theatlantic.com/photo/2014/12/bhopal-the-worlds-worst-industrial-disaster-30-years-later/100864/.

# 4.3 AIR QUALITY IMPACT – ON HEALTH AND THE ENVIRONMENT

Both PM and gas air pollutants have effects on human health, *impacts*, and can affect human and biosystem welfare—property, enjoyment of life and conduct of business, or the ecosystems of animals, vegetation, and other living creatures. People use and are exposed to many poisonous substances, toxic air or water pollutants, constituents of food,<sup>22</sup> although the likelihood, or risk, of most of these chemicals being present in harmful quantities for a harmful period of time is low.

Each organ of the body handles part of the chemistry needed to sustain life and grow. Biological creatures have evolved many protective mechanisms and protect cells by filtering, neutralizing, or blocking most harmful substances in some way. Some compounds are contained and removed as waste. Pollutant doses must generally exceed a threshold quantity before harm is done.

Several factors contribute to the health impact and risk of air pollution. As summarized in later sections of this chapter, each of the criteria pollutants, and some others, has a dossier of health effects.

- 1. specific chemicals have different effects.
- 2. higher concentrations cause more harm.
- 3. chemicals may react to form new compounds that may cause unexpected or indirect effects.

Some of the health and welfare effects can be attributed to the specific chemical composition of organic contaminants and particles. In the case of *extremely hazardous substances* (EHS), very short exposures can be deadly.

Health and welfare impacts can occur at a wide range of concentrations. Air contaminants are usually dispersed in the atmosphere in parts per million volume concentrations (or mg/m³) or less. In general, older adults and children are more affected than healthy adults by air quality with lower pollutant concentrations. Children's respiratory systems are still developing and they breathe more air (and air pollution) per kilogram of body weight than adults. Children and other people active outdoors have a higher exposure to ambient pollutant concentrations, <sup>23</sup> but even

<sup>&</sup>lt;sup>22</sup>US EPA. Technology Transfer Network – Air Toxics Website, Risk Assessment for Toxic Air Pollutants: A Citizen's Guide, EPA 450/3-90-024, March 1991, https://www3.epa.gov/airtoxics/3 90 024.html.

<sup>&</sup>lt;sup>23</sup>US EPA. NOAA, et al, How Smoke from Fires Can Affect Your Health, https://www.airnow.gov/index.cfm?action=smoke.index, (accessed January 12, 2017).

indoors, concentrations of combustion emissions, CO and NO<sub>2</sub>, can be elevated to unhealthy concentrations, due to gas stove or fossil fuel heating furnace emissions.

A high concentration of any chemical that displaces enough  $O_2$  to lower the concentrations below eight percent can cause *asphyxiation*, death from lack of oxygen, in eight minutes. Coordination is seriously affected at  $O_2$  concentrations below 15 percent.<sup>24</sup> As in the Lake Nyos event described at the beginning of this chapter, large natural releases of  $CO_2$  from volcanos or other emissions with heavier chemical weight than  $N_2$  and  $O_2$  can create locally oxygen-deficient conditions that are toxic.

Finally, pollutant chemical effects are often amplified by the presence of water in the atmosphere or the lung. At high concentrations, exposure to the acid solutions made from CO, NOx, SO<sub>2</sub>, and sulfate and nitrate PM harms body tissues. Water also assists in transforming chemicals into secondary pollutants with additional health and welfare effects. Other chemical reactions can amplify or decrease its effects.

Health risks are a function of the *exposure* and the *dose*. The body must be exposed to the contaminant at a location on or in the body from which a *dose*, or quantity, of the chemical can be delivered and cause harm. The dose may directly react with or change tissue in a negative way or the chemical can be passed through to internal systems. The health risk of the same pollutant usually increases as the exposure period is lengthened and the body receives a larger dose. Exposures affect lung function in both brief short-term periods and long-term timeframes. Short-term exposures at high concentrations of EHS pollutants can be deadly

The duration of health effects may be immediate and short or last for a long period as well. *Acute* health effects, immediate harmful impacts, include symptoms such as airway irritation, coughing, asthma attacks difficulty breathing, increased mucus production, or aggravated symptoms of respiratory diseases. *Chronic effects* can be seen in organ or functional impairment over the long-term and include cancer. They often, but not always, result from long-term or repeated exposures at relatively low concentrations. Both acute and chronic effects of some pollutants can result in death.

Each breath of polluted air brings a dose of contaminant into the body. When air pollutants are inhaled, the air passageways and lungs are exposed directly to potential harmful effects from the contaminant. Direct

<sup>&</sup>lt;sup>24</sup>OSHA. Letter to FirePass Corp, CFR 1910.134 Respiratory Protection Standard (d (2 (iii). https://www.osha.gov/pls/oshaweb/owadisp.show\_document?p\_id=25743&p\_table=INTERPRETATIONS.

exposure to some pollutants in the ambient air can also affect the skin or eye membrane.

Breathing takes gases and the smallest PM into the deepest part of the lung, the alveoli, where pollutants can be absorbed into the blood stream and then affect any of the body organs or cell activities. Although air intake varies significantly between children and adults and people at rest inhale less air than those performing physical activities, a default inhalation value for a 70-kg human adult is approximately 13.8 liters of air per minute. At an ambient CO concentration of 35 ppmv, the CO dose in one hour would be approximately 0.033 g. Health studies use a metric reference dose (RfD) of chemical per body mass per day, and in this instance, if the CO concentration were constant for 24 hours, the dose would be 0.0114 mg/kg per day.

The dose and exposure mechanisms for impacts on environmental and human welfare are the same, except that the environment has more water and soil *pathways*, routes for exposures to chemicals that have harmful impacts. PM contaminates the water and ground when deposited, and the acidity created by secondary combustion air emissions corrodes materials or can present harmful exposures to biota. This type of effect on an ecology, a system of living creatures, their food, and water environment, will continue long after the polluted air has dispersed.

## 4.4 AIR QUALITY STANDARDS

Primary NAAQS concentrations define acceptable, ambient air quality concentrations that protect human health with an adequate margin of safety. Secondary standards are designed to protect public welfare. As referenced in Chapter 3, the EPA Air Quality Criteria documents<sup>26</sup> as well as the background Integrated Science Assessments (ISA)<sup>27</sup> provide an extensive overview of health effects, material damage, and typical exposures and health risk assessments. Technical information on the USEPA studies and reviews for all the criteria pollutants are linked to the webpage https://www.epa.gov/naaqs. The U.S. Occupational Safety and

<sup>&</sup>lt;sup>25</sup>US EPA, Risk Assessment Home, https://www.epa.gov/risk/human-health-risk-assessment. Methods for Derivation of Inhalation Reference Concentrations and Application of Inhalation Dosimetry, EPA 600/8-90/066F October 1994, https://www.epa.gov/risk/methods-derivation-inhalation-reference-concentrations-and-application-inhalation-dosimetry.

<sup>&</sup>lt;sup>26</sup>US EPA. Criteria Air Pollutants, https://www.epa.gov/criteria-air-pollutants, (accessed March 17, 2017).

<sup>&</sup>lt;sup>27</sup>US EPA. Integrated Science Assessment for Oxides of Nitrogen – Health Criteria (Final Report, 2016), https://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=310879.

Health Administration (OSHA) has air quality limits for air pollutants over an 8-hour period designed to protect the health of workers in the work-place.<sup>28</sup> The European Commission (EC), the United Nations (U.N.), and most countries have standards or guidelines for acceptable air quality in their own territory.

Primary AAQS are shown in Table 4.1. In the United States, criteria pollutants have secondary standards with the exception of  $CO_2$ . The secondary NAAQS concentrations are the same as the primary standards, except that the  $PM_{2.5}$  annual secondary standard (15  $\mu$ g/m<sup>3</sup>) is higher than the annual primary standard (12  $\mu$ g/m<sup>3</sup>).

**Table 4.1.** National ambient air quality standards <sup>29 30</sup>

	U.S. NAAQS		EC AQS	
Pollutant	Primary standard	Averaging period	Standard	Averaging period
Ozone	0.07 ppm	8 hour	120 μg/m <sup>3</sup>	8-hour mean
$PM_{10}$	$150 \ \mu g/m^3$	24 hour	$50~\mu g/m^3$	24 hour
PM <sub>2.5</sub>	$12 \mu g/m^3$	Annual	$25~\mu g/m^3$	annual
PM <sub>2.5</sub>	$35 \mu g/m^3$	24 hour	$350~\mu\text{g/m}^3$	1 hour
CO	9 ppm	8 hours	$10 \text{ mg/m}^3$	8-hour mean
	35 ppm	1 hour		
$SO_2$	75 ppb	1 hour	$350~\mu\text{g/m}^3$	1 hour
$NO_2$	53 ppb	annual	$40~\mu g/m^3$	annual
$NO_2$	100 ppb	'1 hour	$200~\mu g/m^3$	24 hour

<sup>&</sup>lt;sup>28</sup>US Department of Labor, Occupational Safety and Health Administration, 29CFR1910.1000, Toxic and Hazardous Substances, Table Z-1 Limits for Air Contaminants, https://www.osha.gov/pls/oshaweb/owadisp.show\_document?p\_table=STANDARDS&p\_id=9992.

<sup>&</sup>lt;sup>29</sup>US EPA. NAAOS Table, https://www.epa.gov/criteria-air-pollutants/naags-table.

<sup>&</sup>lt;sup>30</sup>EC, Environment, Air Quality Standards, http://ec.europa.eu/environment/air/quality/standards.htm.



EPA has developed the Air Quality Index (AQI), a value that calculates the combined health risk of poor air quality and can notify the public in a simple and clear way about acutely harmful pollutant levels for each day. Because many U.S. and state government agencies monitor air quality, a group of agencies now collaborates to maintain the AQI and the <a href="https://www.airnow.com">www.airnow.com</a> website. The AQI evaluates the O<sub>3</sub> and PM<sub>2.5</sub> concentrations on a daily basis. AQI values of 50 or less define good air quality. If concentrations are, or are predicted to be, above the ambient standards, the AQI will be greater than 100. The AQI levels are color-coded.

The website explains health and welfare impacts in plain English and has a link to a brochure that can be downloaded and printed. The AQI warning chart for PM, shown in Table 4.2, has virtually the same information as the one for  $O_3$ .

AirNow has a wealth of air pollutant health information, with links to its partners, to visibility webcams, and to education resources, among others. International AQI related websites are also linked, including most of the European Countries and monitors at U.S. Embassies, and in China, Thailand, Australia, Canada, and Mexico.

<sup>&</sup>lt;sup>31</sup>US National Oceanographic, Atmospheric Administration, USEPA. US National Park Service and local agencies, AirNow Website, https://www.airnow.gov, based on data submitted to the USEPA Air Quality System.

<sup>&</sup>lt;sup>32</sup>AirNow. Air Quality Index Brochure, https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P1001EX6.txt, (accessed July 7, 2017).

<sup>&</sup>lt;sup>33</sup>AIRNOW. Air Quality Index Basics, https://cfpub.epa.gov/airnow/index.cfm?action=aqibasics.aqi, (accessed November 26, 2016).

Good	[green]	0-20	None
Moderate	[yellow]	51-100	Unusually sensitive people should consider reducing prolonged or heavy exertion
Unhealthy for Sensitive Groups	[orange]	101-150	101–150 People with heart or lung disease, older adults, and children should reduce prolonged or heavy exertion.
Unhealthy	[red]	151–200	151–200 People with heart or lung disease, older adults, and children should avoid prolonged or heavy exertion. Everyone else should reduce prolonged or heavy exertion
Very Unhealthy Alert	[purple]	201–300	201–300 People with heart or lung disease, older adults, and children should avoid all physical activity outdoors. Everyone else should avoid prolonged or heavy exertion.
Hazardous	[dark red]		301–500 Everyone: Avoid all physical activity outdoors.  Sensitive groups: Remain indoors and keep activity levels low. Follow tips for keeping particle levels low indoors.

<sup>&</sup>lt;sup>34</sup>AIRNOW. Particle Pollution and Your Health, https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=P1001EX6.txt Air Quality Guide for Particle Pollution, https://www.airnow.gov/index.cfm?action=pubs.aqguidepart, AirNow.

## 4.5 HUMAN HEALTH EFFECTS

The EPA studies health risks from environmental contaminants and concentrations, and OSHA<sup>35</sup> and the National Institute for Occupational Safety and Health (NIOSH) research contaminant risks in workplaces and buildings. NIOSH has determined concentrations of many pollutants that are *immediately dangerous to life and health* (IDLH).<sup>36</sup> Both organizations study chronic and lethal health effects from long-term exposures that cause organ damage or diseases that cannot be healed or repaired. The risk of developing various forms of cancer is often increased by exposure to low concentrations of HAPs over a period of many years or a lifetime.

Poor air quality will affect sensitive people, older adults, children, and people with heart or respiratory disease, more and at lower concentrations than healthy adults. Pollutants place additional health stress on people with reduced lung function, and the many children with asthma fall into this group. Pollutants can affect the development of a child's respiratory system as it matures. The dose of pollutants that children receive is larger in proportion to their body weight than an adult and they may breathe more ambient air and pollution if they are more active outdoors.<sup>37</sup>

The elevated number of visits to emergency rooms for respiratory problems during episodes or on poor air quality days is often used as a conservative metric for the intensity of an episode.<sup>38</sup>

## 4.5.1 PM<sub>2.5</sub> RESPIRATORY EFFECTS

Physical size of the PM determines whether human health effects occur from exposure to the airways or occur deeper in the lung and throughout the body. The human nose filters out large TSP, particles >10 µm, and with the exception of the HAP As, large TSP is not of great health concern.

<sup>&</sup>lt;sup>35</sup>Occupational Safety and Health Administration, Safety and Health Topics: Listing, https://www.osha.gov/SLTC/text\_index.html, (accessed June 16, 2017).

<sup>&</sup>lt;sup>36</sup>National Institute for Occupational Safety and Health, *Immediately Dangerous To Life or Health (IDLH) Values*, https://www.cdc.gov/niosh/idlh/default.html, (accessed June 16, 2017). <sup>37</sup>US EPA. ISA for Particulate Matter (Final Report, Dec 2009), Washington, DC, EPA/600/R-08/139F, 2009, https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=216546.

<sup>&</sup>lt;sup>38</sup>US EPA. 42 CFR 410.4 and 5, National Primary and Secondary Ambient Air Quality Standards, Notice of Rulemaking, Federal Register, Volume 36, Number 84, page 8186 et seq., April 30, 1971, https://www3.epa.gov/ttn/naaqs/standards/so2/previous/1971-april30 -final-36fr8186.pdf.

Nonetheless, when any PM irritates the airways, it can cause coughing or difficulty breathing.

 $PM_{10}$  is inhaled into the lung. The smallest particles,  $PM_{2.5}$ , are so small and light that they are caught in Brownian motion, unaffected by air currents, and are only randomly expelled from the lungs when breath is exhaled. Because it stays in the lungs longer than coarse  $PM_{10}$ ,  $PM_{2.5}$  has the most significant health effects.

PM health effects are associated with both 24-hour and annual average exposures.<sup>39</sup> The NAAQS update in 1987 first identified PM<sub>10</sub> as the pollutant of concern rather than TSP. Even though PM<sub>10</sub> is a subset of TSP, only the annual average concentration was made stricter in the update than the original TSP NAAQS, and this implies that the TSP 24-hour health effects identified in 1971 were actually related to the smaller PM<sub>10</sub>. The secondary limits were raised to match the primary limits. The studies and NAAQS revisions are summarized in Table 4.3.

## Table 4.3 Criteria studies and NAAQS for PM emissions

1969 U.S. Health, Education and Welfare Department, Public Health Service published the first Air Quality Criteria for Particulate Matter and Air Quality Criteria for Sulfur Oxides.

1970 U.S. EPA published an update to the Air Quality Criteria for Particulate Matter and Air Quality Criteria for Sulfur Oxides in the first few months of its existence.

1971 Initial Primary and Secondary TSP NAAQS issued. 40

1977 The Air Quality Criteria document (3 volumes) was updated in response to specific requirements of Section 108 of the Clean Air Act, as amended in 1977.

1982 U.S. EPA published an update to the Air Quality Criteria for Particulate Matter and Sulfur Oxides.

1987 PM<sub>10</sub> replaced TSP as the regulated NAAQS pollutant.

1997  $PM_{2.5}$  Primary and Secondary NAAQS limits added, more than 50% lower than the  $PM_{10}$  NAAQS.

<sup>&</sup>lt;sup>39</sup>USEPA. PM Effects Information, https://www.epa.gov/pm-pollution/health-and-environmental-effects-particulate-matter-pm.

<sup>&</sup>lt;sup>40</sup>USEPA. Table of Historical PM NAAQS, https://www.epa.gov/pm-pollution/table-historical-particulate-matter-pm-national-ambient-air-quality-standards-naaqs, (accessed July 7, 2017). Formerly, https://www3.epa.gov/ttn/naaqs/standards/pm/s\_pm\_history.html.

Health effects may also be caused by the specific chemical composition of each particle.<sup>41</sup> A good example of a harmful PM constituent is the HAP asbestos (As). Inhaled asbestos fibers become embedded in and irritate the lung lining. They are known to be a cause of the cancer mesothelioma.<sup>42</sup> Metals and other constituents of PM can cause additional harm if they are soluble in the lung mucus lining and could, therefore, be absorbed into the bloodstream and transferred to target organs.

The effect of PM and other pollutants on a population can be interpreted through studies which determine how much higher the mortality rate is in polluted areas. In 2005 in the United States, an estimated 21,000 deaths occurred *prematurely*, over and above natural causes, due to electric generating unit (EGUs) emissions. A 2013 study of PM<sub>2.5</sub> pollution from coal-burning sources in China estimated that 155,000 premature deaths were caused by industrial emissions and 86,500 deaths from power generation. 44

## 4.5.2 SOx, NOx, AND CO HEALTH IMPACTS

Aside from the effects of the oxidized PM<sub>2.5</sub> generated from NO<sub>2</sub> and SO<sub>2</sub>, these gases have acute health impacts due to high 1-hour concentrations as well as more lasting impacts from annual exposure to lower concentrations.

When  $SO_2$  levels are at the 24-hour NAAQS or higher, studies show that bronchitis is aggravated and daily mortality increases. People with asthma who are exercising show increased airway resistance within an hour if they are not using preventative medicine.<sup>45</sup>

In 2010, a new, 1-hour NAAQS for NO<sub>2</sub> was issued based on a new EPA ISA to protect sensitive people from the NO<sub>2</sub> emissions and concentrations

<sup>&</sup>lt;sup>41</sup>USEPA. Particulate Matter Basics, https://www.epa.gov/pm-pollution/particulate-matter-pm-basics, (accessed November 25, 2016).

<sup>&</sup>lt;sup>42</sup>National Institutes of Health, National Cancer Institute, Asbestos Exposure and Cancer Risk webpage, https://www.cancer.gov/about-cancer/causes-prevention/risk/substances/asbestos/asbestos-fact-sheet, (accessed April 23, 2017).

<sup>&</sup>lt;sup>43</sup>S.L. Penn, S. Arunachalam, M. Woody, W. Heiger-Bernays, Y. Tripodis, and J.I. Levy. "Estimating State-Specific Contributions to PM2.5- and O3-Related Health Burden from Residential Combustion and Electricity Generating Unit Emissions in the United States." *Environmental Health Perspectives* 125, pp. 324–332; 2017 March, http://dx.doi.org/10.1289/EHP550; https://ehp.niehs.nih.gov/EHP550.

<sup>&</sup>lt;sup>44</sup>Health Effects Institute. "Burden of Disease Attributable to Coal-burning and other Air Pollution Sources in China." *Global Burden of Disease, Major Air Pollution Sources project (GBD MAPS)*, August 2016, https://www.healtheffects.org/publication/burden-disease-attributable-coal-burning-and-other-air-pollution-sources-china, (accessed July 12, 2017).
<sup>45</sup>USEPA. "Proposed Decision not to Revise the NAAQS for Sulfur Oxides." 53FR80, April

<sup>&</sup>quot;\*\*\*USEPA. "Proposed Decision not to Revise the NAAQS for Sulfur Oxides." 53FR80, April 26, 1988, page 14932, https://www3.epa.gov/ttn/naaqs/standards/so2/previous/19930421fr.pdf.

due to high traffic roadways. Short-term exposure to  $NO_2$  affects people with asthma and is a risk to the respiratory health of others. Studies suggest that both short- and long-term exposures also impact cardiovascular health and affect mortality. Other health studies indicate that long-term  $NO_2$  exposures may affect reproductive health and development of cancer. <sup>46</sup>

As a precursor chemical in ambient photochemical reactions,  $NO_2$  also contributes to high ozone levels, which causes respiratory system and other health effects.<sup>47</sup>

CO is harmful to humans and other animals because it blocks the receptors in red blood cells that accept oxygen, and as a result, sufficient  $O_2$  cannot be circulated to the heart, brain, other organs or cells. <sup>48</sup> One symptom from reduced oxygen levels is chest pain. At levels in the 2,000  $\mu g/m^3$  range, CO causes unconsciousness and lethal asphyxiation. CO can be elevated near roadways and in enclosed areas, both ambient and indoors. <sup>49</sup>

#### 4.5.3 OZONE HEALTH IMPACTS

The high-energy criteria pollutant  $O_3$  has health effects on different tissues and organs in the body. High concentrations of ozone generally do not last for more than an 8-hour cycle, during warm, sunlit days. Both primary and secondary NAAQS are based on an 8-hour average. High  $O_3$  levels occur in photochemical smog reactions in ambient air along with many specific OC compounds, such as polycyclic aromatics and other organic intermediate byproducts. These individual chemicals often have other, direct, specific health impacts.

The most recent ISA  $(2013)^{50}$  indicates that  $O_3$  causes airway constriction, with symptoms ranging from shortness of breath, wheezing, and aggravation of the respiratory diseases of bronchitis, emphysema, and asthma. The harmful effects can continue without symptoms, and  $O_3$  can

<sup>&</sup>lt;sup>46</sup>USEPA. Integrated Science Assessment for Oxides of Nitrogen - Health Criteria, January 2016, https://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=310879, (accessed June 19, 2017).
<sup>47</sup>US EPA. Basic Information about NO<sub>2</sub>, https://www.epa.gov/no2-pollution/basic-information-about-no2#Effects.

<sup>&</sup>lt;sup>48</sup>USEPA. Basic Information about Carbon Monoxide (CO) Outdoor Air Pollution, https://www.epa.gov/co-pollution/basic-information-about-carbon-monoxide-co-outdoor-air-pollution#Effects.

<sup>&</sup>lt;sup>49</sup>USEPA. Reviewing NAAQS, CO Air Quality Standards, https://www.epa.gov/naaqs/carbon-monoxide-co-air-quality-standards.

<sup>&</sup>lt;sup>50</sup>USEPA. Integrated Science Assessment for Ozone and Related Photochemical Oxidants, EPA 600/R-10/076F, February 2013, https://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=247492.

cause obstructive pulmonary disease (COPD) and has been shown to have chronic effects on the lung development of children.<sup>51</sup>

#### 4.5.4 LEAD AND HAP HEALTH IMPACTS

Pb (lead) is known to have toxic effects on three important body systems, the brain and nervous system, the blood-making system in the bone marrow, and the kidneys. The impact and health effect are measured by Pb concentrations in the blood, which are related to doses and exposure from both the air and from ingested food, dust, and water contaminated with lead. Young children (ages 1 to 5) are particularly susceptible to lead because it damages their developing brains and is stored in their growing bones.

Elevated ambient concentrations contribute significantly to the blood Pb levels known to harm children. The initial NAAQS for Pb was issued in 1978,<sup>52</sup> and after new health studies became available, the standard was reduced to 10% of its initial value in the early 1990s.

Many specific chemicals have toxic effects on human health and have been addressed through different approaches than the programs for ambient air quality of criteria pollutants. Generally, the local exposure levels from emission sources are reviewed in light of known toxicological information. Many states and local air agencies have toxics programs to control compounds of interest in their regions and are authorized to limit emissions if they create unacceptable air (or water) quality that exposes residents to harmful concentrations.

In the United States, the federal government has identified individual airborne chemicals for designation as HAPs based on well-established, scientific knowledge of their hazards. Exposure to HAPs is associated with a variety of acute adverse health impacts, including irritation of the lung, skin, and mucus membranes and digestive system effects such as nausea and vomiting. The effects may also include chronic health disorders such as damage to the central nervous system or kidneys. Many HAPs, including benzene, POM, and asbestos are known to be carcinogenic or mutagenic.

Initially, EPA listed and developed regulations and standards for only a few HAPs,  $^{53}$  and in 1990, the list of HAPs was expanded to 189 chemicals.

 $<sup>^{51}\</sup>text{US}$  EPA  $O_3$  information, https://www.epa.gov/ozone-pollution/ozone-basics#effects. Reviewing NAAQS, O3 Air Quality Standards, https://www.epa.gov/naaqs/ozone-o3-air-quality-standards.

<sup>&</sup>lt;sup>52</sup>US EPA. National primary and secondary ambient air quality standards for lead, 40 CFR50.12, 43FR194 Oct 5, 1978, p. 46246 et seq.

 $<sup>^{53}</sup>https://www.epa.gov/caa-permitting/national-emission-standards-hazardous-air-pollut-ants-region-7.\\$ 

Fact sheets summarizing the specific health impacts of each of the HAPs can be accessed from the EPA Health Effects Notebook for Hazardous Air Pollutants.<sup>54</sup> More detailed information on toxic substances is available from the Agency for Toxic Substances and Disease Registry (ATSDR), a federal public health agency in the U.S. Department of Health and Human Services. The website for toxicological information is https://www.atsdr.cdc.gov/substances/index.asp

The HAP emissions and the sources originally listed are:

- Asbestos: <sup>55</sup> mills, manufacturing, spraying, and demolition and renovation
- Benzene: coke production, equipment leaks, storage vessels, transfer, and waste
- · Beryllium: extraction and processing plants, and from rocket firing
- Inorganic Arsenic: glass manufacturing, primary copper smelters, and arsenic production facilities
- Mercury (Hg): Production
- Radon and Radionuclides: Uranium and phosphorus from phosphorus mines
- Vinyl Chloride: vinyl chloride, polyvinyl chloride, and ethylene dichloride plants

The National Air Toxics Assessment (NATA) by the EPA revealed that 32 HAPs and lead are often found in the air in urban areas at significant concentrations, posing significant health risk to the populations living there. <sup>56</sup> Benzene, Hg, arsenic compounds, trichloroethylene, POM, cadmium, and polychlorinated biphenyls (PCBs) are among the pollutants of concern.

Exposure to benzene increases the risk of leukemia and other blood disorders.<sup>57</sup> Many of the state toxic air pollutant programs have set health thresholds for benzene with a margin of safety, and the concentrations are often 10 to 100 times lower than ambient concentrations in the vicinity of petrol stations, where quantities of the benzene in the fuel have evaporated. Details on benzene cancer risk and information for other chemicals

<sup>&</sup>lt;sup>54</sup>National Institutes of Health (NIH). https://www.epa.gov/haps/health-effects-note-book-hazardous-air-pollutants, (accessed April 23, 2017).

<sup>&</sup>lt;sup>55</sup>S. Mukherjee. (2010). *The Emperor of All Maladies. A Biography of Cancer*. New York: Scribner.

<sup>&</sup>lt;sup>56</sup>US EPA. NATA website, https://www.epa.gov/national-air-toxics-assessment, (accessed July 12, 2017).

<sup>&</sup>lt;sup>57</sup>National Institutes of Health (NIH). https://www.cancer.gov/about-cancer/causes-prevention/risk/substances/benzene, (accessed April 23, 2017).

can be found at the National Institutes of Health, National Cancer Institute webpages.<sup>58</sup>

Inhalation of Hg emissions or absorption through the skin has been shown to harm the nervous system. The felt makers used it to produce felt, and felt hat wearers were exposed to it. In fact, the stories about mad hatters are true.

The major pathway for exposure to arsenic is through food, but short-term exposure to high airborne concentrations can cause nausea, diarrhea, and abdominal pain. Chronic exposure to arsenic, cadmium, and POM can affect the nervous system and irritate the skin. Inorganic arsenic is a human carcinogen. Short-term exposure to cadmium compounds and PCBs can irritate the airways and lungs, and chronic exposure to cadmium and trichloroethylene has been found to be a cause of kidney disease. Cigarette smoke exposes people to cadmium, formaldehyde, POM, and many other HAPs.

### 4.6 WELFARE EFFECTS

Pollutant exposures and PM deposition affect plants, animals, and waterways. Some emissions, including CO<sub>2</sub> and chlorinated synthetic chemicals like Freon<sup>TM</sup>, have long-range effects on the chemistry, clarity, or energy equilibrium of the atmosphere.

## 4.6.1 POLLUTANT IMPACTS ON ANIMALS, PLANTS, AND MATERIALS

Air pollutants affect animal health in some of the same ways they impact human health, but the sensitivity to each pollutant and the exposure and dose relationships will be different for each species. One-cell organisms will not have as many defenses against acidity or chemical toxicity. However, effects on these and slightly more complex, multi-cell organisms without specific organs are not subject to the same "health" risks from carcinogens or other pollutants causing systemic damage.

Plant leaves are damaged by O<sub>3</sub>, other oxidants, and acidic pollution. The effects can include slower growth, impaired photosynthesis, and higher susceptibility to diseases, insects, and other pollutants. The first

<sup>&</sup>lt;sup>58</sup>National Institutes of Health (NIH) Integrated Risk Information System (IRIS). https://toxnet.nlm.nih.gov/cgi-bin/sis/search2. US EPA collects health risk information on HAPS and other toxic pollutants in IRIS, which is maintained by the National Institutes of Health.

research on OC emissions was done as agricultural studies, and these plant researchers were the first to develop methods to monitor air quality and  $\rm O_3$  and OC effects. <sup>59</sup> Exposure to  $\rm NO_2$  and  $\rm SO_2$  puts stress on the leaves and plants as well.

OC emissions from plants, soil micro-organisms, and other biota do not create the same adverse effects that anthropogenic VOC species and emission levels do. Biogenic emissions supplement ecosystem carbon cycles and usually fit into the balance of the cycle. One creature's waste provides food and energy for another one that evolved to fill that niche in the ecology.

TSP impacts the environment when deposited, adding to dusty lands, roads, and sooty windowsills, and it introduces solids into waterways.

The criteria pollutants also affect the built, human environment negatively. Stone and building materials can be stained or degraded by PM, especially the acidic, secondary PM<sub>2.5</sub>. Air with high O<sub>3</sub> concentrations causes damage to rubber and synthetic materials, such as nylon, an early synthetic used widely for women's stockings in the mid-20th century. Exposure to the acidity of SO<sub>2</sub> and NO<sub>2</sub> also affects materials. Damage and discoloration of limestone, metalwork, and statues can be seen in many cities, and maintenance costs can be significant. Although ambient conditions are not the cause, high PM concentrations can also pose a safety risk inside buildings, grain silos, and other structures, because the fine dust can create an explosive atmosphere.

## 4.6.2 LONG-RANGE POLLUTION AND ECOSYSTEM IMPACTS

PM<sub>2.5</sub> can affect people and the environment as it travels or is created hundreds of kilometers from its source.

As discussed in Chapter 3, Section 2,  $PM_{2.5}$  reduces visibility, making the air appear hazy. The long-distance vistas of the Western United States, the "Big Sky" country, had a natural range of 120 to 140 km due to the clean, low humidity air. But many views were noticeably shortened when the big, coal electric plants (EGU) were built and emitted both primary  $PM_{10}$  and secondary  $PM_{2.5}$  from the original  $SO_2$  and  $NO_2$ . The visibility in other wilderness areas, parks and eastern mountains in the United States is often affected by the humidity and biogenic emissions, but the vistas from these once pristine areas are also affected by pollution.

<sup>&</sup>lt;sup>59</sup>CARB. Arie Haagen-Smit, https://www.arb.ca.gov/html/haagen-smit.htm, (accessed November 9, 2016).

Primary and secondary PM<sub>2.5</sub>, much of it from energy generation, affects people and the environment long distances downwind of the source. The pollutants emitted in urban areas and in plumes from EGUs and other major sources may only increase ambient air pollution in those areas slightly, but can have a significant impact on areas downwind without many local sources. A study published in 2014 estimated that SO<sub>2</sub> emitted in China contributes as much as 24% of the sulfate PM<sub>2.5</sub> in the Western United States on spring days with strong westerly winds.<sup>60</sup>

PM<sub>2.5</sub> can serve as a nucleus for water droplet formation in clouds and precipitation. Research indicates that the Northwest Pacific may see as much as a 7% increase in precipitation due to Chinese PM<sub>2.5</sub> air pollution.<sup>61</sup> Precipitation can also absorb PM and other pollutants and scrub them from the air, improving air quality. In Wisconsin, more than 200 rivers and lakes are known to have collected Hg in their waters from the air. Biota may not be lethally poisoned when they eat it, but animals higher up the food chain accumulate and concentrate it, making the fish unsafe for humans to eat. The largest sources of Hg anywhere in range of these waters are coal-burning power plants.<sup>62</sup>

 $Acid\ rain$  is the term used for rain, sleet, and snow that becomes acidic as it washes  $SO_2$ ,  $NO_2$ , and  $SO_4$  and  $NO_3$   $PM_{2.5}$  out of the air. Acid rain and dry deposition can occur more than 1,000 km from the source.

The acidity affects soil, plant root systems, and surface and ground-water. Acidity allows aluminum, Hg, and other metals to become soluble, and when it leaches metals from the rocks and soil, metal organic compounds can be produced that are toxic to root systems, plants, and animals. Because the typical geology and minerals of the Northeast, Southeast, and Western mountain states lack elements to neutralize acidity, these areas and their forests are most affected. Acid rain impacts along the Appalachian Mountains, dead trees, and crystal clear lakes without algae or fish, were some of the first examples of damage determined to be a result of regional scale air quality. Air programs have reduced SO<sub>2</sub> and NO<sub>2</sub> emissions, and nearly three-quarters of the lakes found to be acidified in the 1970s and

<sup>&</sup>lt;sup>60</sup>J. Lin, S. Davis, et al. (2014). "China's International Trade and Air Pollution in the United States." *Proceedings of the National Academy of Science*. doi:10.1073/pnas.1312860111, http://www.pnas.org/content/111/5/1736.

<sup>61</sup> Ibid.

<sup>&</sup>lt;sup>62</sup>Union of Concerned Scientists. Coal vs. Wind, http://www.ucsusa.org/clean\_energy/coalvswind/brief\_coal.html#.WFdD41wjrcQ, (accessed November 2016).

<sup>&</sup>lt;sup>63</sup>U.S. EPA. Integrated Science Assessment (ISA) for Oxides of Nitrogen, Oxides of Sulfur and Particulate Matter - Ecological Criteria (Final Report, Dec 2008). U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-08/082F, 2008, https://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=201485. Executive Summary can be downloaded from that page.

1980s have recovered. However, forests, soils, and ecosystems have not been as resilient to date.

Ecosystems are affected by changes in the nitrogen cycle which operates between physical and biological systems, and NO<sub>2</sub> emissions and ammonia deposition alter the underlying nitrogen/carbon balance and transfers. The amount of nitrogen deposition has increased by 1000 percent since the Industrial Revolution began;<sup>64</sup> in 2004 to 2006, the deposition rate in the upper Midwestern United States was over 9 kg nitrogen per hectare per year.<sup>65</sup> Water pathways bring the extra nitrogen load to soils, wetlands, freshwater, and estuarine ecologies. The carbon/nitrogen balance changes cause increases in methane production and change the plant and related animal biodiversity. When nitrogen is enriched, plant growth can be increased, which may weaken the plants or fill surface waters with algae and other simple cell organisms, a process known as *eutrophication*.<sup>66</sup>

The worst impact of environmental pollution occurs when it harms populations of organisms and vegetation in an ecosystem to the extent that they decline significantly or die off. The loss of biodiversity seriously disrupts the balance and food cycles and can make an ecosystem collapse. When new species invade, food and water resources can be overtaxed or polluted with new wastes that the ecosystem cannot use or process.

In the 1980s, scientists found a class of very stable, synthetic chemicals destroying a protective gas layer in the atmosphere approximately 22 km above the surface of the earth. At this elevation, the energy from some of the most energetic and harmful rays of the sun, *ultraviolet* (UV) radiation, is absorbed as it converts O<sub>2</sub> into a thin layer of high-energy O<sub>3</sub> molecules. This *ozone layer* naturally reduces the radiation reaching the ground and protects terrestrial ecologies from high levels of solar radiation. However, the O<sub>3</sub> facilitates reactions that break down the stable synthetic chemicals, including chlorinated fluorocarbon compounds (CFC), or halons, carbon compounds with other halogen elements. The reactions deplete the O<sub>3</sub>, leaving a hole in the protective ozone layer that allows damaging levels of UV radiation to pass through. Over 25 years, international action to significantly limit emissions of CFCs, including CFC-11, CFC-12, and Freon, R-22, and others, has regenerated most areas of the layer that had been missing.

<sup>&</sup>lt;sup>64</sup>US Oak Ridge National Laboratory, Global Maps of Atmospheric Nitrogen Deposition, 1860, 1993, and 2050, https://daac.ornl.gov/CLIMATE/guides/global\_N\_deposition\_maps. html, (accessed October 11, 2017).

<sup>&</sup>lt;sup>65</sup> U.S. EPA. Integrated Science Assessment (ISA) for Oxides of Nitrogen and Sulfur - Ecologi-cal Criteria (Final Report, Dec 2008). U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-08/082F, 2008, https://cfpub.epa.gov/ncea/isa/recordisplay.cfm?deid=201485.

<sup>&</sup>lt;sup>66</sup>US EPA. Nutrient Pollution, https://www.epa.gov/nutrientpollution, (accessed November 8, 2017).

## 4.6.3 CLIMATE CHANGE AND GLOBAL SCALE WELFARE EFFECTS

As anthropogenic emissions increase and synthetic chemicals proliferate, air pollution is affecting the balance of physical and biological systems on a global scale.

Global Warming is occurring at a rapid rate (geologically), and research shows that it is primarily a result of fossil fuel emissions dramatically increasing the amount of  $CO_2$  in the atmosphere. As discussed in Chapter 3,  $CO_2$  is a natural component of oxidation and photosynthesis and was long believed to be an innocuous part of the atmosphere.

Heat radiated from the surface of the earth is trapped by CO<sub>2</sub> and other gases in the atmosphere and warms the planet instead of being released into space. The process is known as a *greenhouse effect* and the gases contributing to it are called *greenhouse gases* (GHG). The carbon cycle is dynamic, and plants respond to an increase in CO<sub>2</sub> by growing more and *sequestering*, storing, the carbon as plant material. This CO<sub>2</sub> warming process has happened several times in the geological history of earth, with climate changing over millions of years, accompanied by vast changes in ecosystems.

The average, ambient CO<sub>2</sub> concentration was approximately 400 ppmv in 2016—42 percent higher than the concentration present at the beginning of the Industrial Revolution.<sup>67</sup> The concentration increase over the preceding 8,000 years was 20 ppmv. Coal was an easy addiction for a society craving energy but each increase in consumption of coal or other fossil fuels corresponds directly with an increase in CO<sub>2</sub> emissions. The U.K. used approximately 70 million Mg of coal per year in 1859,<sup>68</sup> the year Darwin's theory of evolution was published. The world population was 1.3 billion people. People were just beginning to learn that emissions were not just visible smoke but tiny, solid particles, and gases made from an array of 92 elements. Scientists had little understanding of the carbon, water and nitrogen cycles that ecosystems depend on.

A century later, in 1960, 3 billion people were living on planet earth.<sup>69</sup> The U.K. was burning approximately 200 million Mg of coal annually.

<sup>&</sup>lt;sup>67</sup>International Panel on Climate Change (IPCC), Fourth Assessment Report: Climate Change, 2007, Working Group I: The Physical Science Basis (WG1), Technical Summary TS.2.1.1 Changes in Atmospheric Carbon Dioxide, Methane and Nitrous Oxide, https://www.ipcc.ch/publications\_and\_data/ar4/wg1/en/tssts-2-1-1.html.

<sup>&</sup>lt;sup>68</sup>United Kingdom, Department for Business, Energy & Industrial Strategy, Statistical data set Historical coal data: coal production, availability and consumption 1853 to 2015, https://www.gov.uk/government/statistical-data-sets/historical-coal-data-coal-production-availability-and-consumption-1853-to-2011.

<sup>&</sup>lt;sup>69</sup>U.S. Census Bureau. International Programs, International Data Base, Revised: September 27, 2016 Version: Data:16.0804 Code:12.0321, https://www.census.gov/population/international/data/idb.

Between 1990 and 2014, China increased annual coal consumption for electricity, heat plants, and combined heat and power from 300 million Mg to 2,070 million Mg.<sup>70</sup>

Physical and ecosystems are adapting to the changing modern carbon and water cycles and climate. Plants are adapting to the extra CO<sub>2</sub> in the air with more growth, and may be sequestering as much as 5% of the anthropogenic emissions. The oceans continue to absorb CO<sub>2</sub> emissions, approximately one-third of the emissions annually over the last four decades.<sup>71</sup>

However, ecosystems and natural cycles are facing added stress from human activities. Enormous tracts of forest that sequester carbon have been cut down, and more land put into cultivation. The synthetic fertilizer that produces increased crop production has become a new area source of the nitrogen compound  $N_2O$ , a GHG with more warming potential than  $CO_2$ .

Atmospheric observations detected an upward trend of  $\mathrm{CO}_2$  concentration starting in the 1960s. At the same time, biologists began to notice that the range of ocean and terrestrial southern species was extending further north as the decades progressed.<sup>72</sup>

Geologically rapid changes in sea level, ocean currents, sea and land temperature, and extreme weather have serious implications.

The year 2016 was the warmest on record since 1880, taking the "title" of hottest year from the year before. The average temperature was 6.8% warmer than the global average from the mid-20th century. The major ocean current in the Pacific was 0.6°C above the mid-20th century average, near its record high temperature, and the average temperature on land in March 2016 was higher than any other month on record, some 2.35°C higher than the mid-20th century average.

As per the discussion of climate and atmospheric energy balancing in Chapter 6, the extra heat in the atmosphere creates more storms, and more extreme weather occurs when the heat exchange is driven by a higher temperature gradient between air masses. Normal locations where the atmosphere is saturated with water and generates clouds will change depending on the heat transfers, and precipitation locations and quantities will change as well, causing drought and floods.

<sup>&</sup>lt;sup>70</sup>UN Energy Statistics Database. Revised: September 27, 2016 Version: Data:16.0804 Code:12.0321, http://data.un.org/Data.aspx?d=EDATA&f=cmID%3ACL.

<sup>&</sup>lt;sup>71</sup>IPCC. Fourth Assessment Report: Climate Change, 2007, WG1, Technical Summary TS.2.1.1 Changes in Atmospheric Carbon Dioxide, Methane and Nitrous Oxide, Table TS-1 Global Carbon Budget, https://www.ipcc.ch/publications\_and\_data/ar4/wg1/en/tssts-2-1-1. html.

<sup>&</sup>lt;sup>72</sup> R. Carson. (1951). *The Sea Around Us*. Oxford University Press.

The oceans also absorb extra heat trapped in the atmosphere and have already expanded, contributing to sea level rise. While it is not certain how warmer oceans will change the world-wide circulation system, the increase in stored heat is but one of several factors that may change them dramatically. Over the last 15,000 years, people and ecologies in northern Europe have adapted to the warm temperatures brought by the Gulf Stream. Studies of ancient oceans show that in past geological eras, the Gulf Stream of the Atlantic Ocean has stopped or changed direction, cooling Europe, and it could happen again.

The warmer atmosphere, with temperatures increasing faster at the north and south poles, is melting the great masses of glacial ice that lock up most of the world's fresh water. This will also contribute to a rising sea. For this reason and the precipitation changes discussed above, the U.S. flood maps for 100 and 500-year flood levels have been changed because flooding historically occurring every 100 years has become much more common over the past 20 to 40 years. A 6,000 km² section of the Antarctic Larsen C Ice Shelf, 50% as large as the country of Jamaica, broke off and floated away in July 2017. It reaches 30 m above the surface of the ocean and is expected to melt completely in about eight years.<sup>73</sup>

The rapid pace of GHG increases and warming have significant impacts on the global biosphere. Higher sea levels and storms will flood the coastal areas and cities. The oceans are becoming more acidic from the additional  $\mathrm{CO}_2$  in circulation that had been buried deep underground as fossilized carbon. This pollution is harming the health of marine ecosystems. During all the previous warming periods, there were no humans depending on agriculture for food, growing plants under conditions with just the right amount of water, sunlight, and nutrients. If the Gulf Stream stops, new systems for agriculture and building heating need to be ready to feed and shelter the population of northern Europe.

Air Pollution is more than chemical contamination, and air quality influences everyone.

 $<sup>^{73}</sup> National Public Radio. Antarctic Shelf Breaks Off, news article, July 12, 2017, http://www.npr.org/sections/thetwo-way/2017/07/12/536818782/massive-iceberg-breaks-free-in-antarctica.$ 

## PREVENTING AIR POLLUTION

## 5.1 ADDRESSING EARLY AIR QUALITY PROBLEMS

Nature, agriculture, and dust affected the local air quality for early humans, who were using peat and wood fuels. Both air and water pollution was made in the process of animal husbandry, and feet and wheels kicked up dust as people travelled dry roadways.

People were bothered by the nuisance caused by nearby sources of pollution, but it had to be balanced with the necessity of sometimes noisome businesses and activities. Over the ages, kings and courts issued decrees to settle local disputes on smoke, odors, and other emission-caused nuisances. Pig farming was generally deemed necessary, although on occasion, the odorous activity would be banished.

When more people gathered into larger communities, they burned more carbon fuels in those densely populated areas to produce energy.

Inefficient coal combustion generated clouds of dark, black smoke. Boiler design engineers and builders were looking for technologies and measures to increase the efficiency of coal combustion and, thus, reduce smoke. Researchers in St. Louis and Illinois, among others, were discovering the first control measures—burning different types of coal, reducing the size of chunks of coal and engineering new furnace designs. Furnace and boiler design engineers invented new ways of processing coal and feeding it to a combustion chamber so it would burn more cleanly. These fuel and equipment design improvements significantly reduced the output of black smoke and the amount of particulate material per unit of energy used—the emission rate. These emission sources were as clean as possible with the current technology. Factories, homes, and transportation would install these clean equipment technologies as soon as reasonable, depending on economic or space and renovation conditions needs.

Cities began to issue smoke prohibition ordinances in the late 19th century, to tackle the unacceptable levels of smoke from coal stoves and boilers. In 1881, the City of Chicago passed a municipal ordinance regulating smoke, which addressed and prevented some of the rising number of individual suits regarding smoke nuisance. Many Sanitation, Health, or Fire Departments began to issue licenses for boiler installations and operators, in part to keep airborne contaminants from causing a nuisance, being harmful, or interfering with the reasonable enjoyment of life and property.<sup>2</sup>

The Municipal Sanitation Departments had another issue affecting air quality, which required management to prevent air impacts—wastes. While most cities had constructed sewers to discharge the human waste stream to the nearby rivers and harbors, the streets were full of dung from horse-drawn carriages, wagons, and streetcars. Early automobiles and trucks had sooty, smelly exhausts, but gas and diesel-fueled vehicles were a big improvement from horse-power, in part because they did not have the odorous, messy solid waste.

As in many U.S. cities in the same period, Philadelphia<sup>3</sup> passed an ordinance in 1904 limiting smoke from chimneys, stacks, flues, or open spaces and defining an unacceptable level of smoke darkness. The ordinance allowed for penalties for non-compliance. The City assigned the program enforcement to its Bureau of Boiler Inspectors, which already had the job of licensing boiler equipment in an attempt to prevent boiler explosions. Ordinances also restricted types of boilers and types of coal and other fuels. By 1920, more than 150 U.S. municipalities had smoke ordinances and 40 of these had smoke abatement departments.<sup>4</sup>

Emission measurement techniques were elusive, but in the works. An early and very public method of environmental monitoring and awareness was developed by architectural engineer Maximilien Ringelmann in 1897. He created a printed chart that visually showed five levels of gray, with grid images made of increasingly thicker, black lines. The darkness of a smoke plume could be visually compared to the charts to determine a

<sup>&</sup>lt;sup>1</sup>A. C. Stern, and Emeritus Professor. (1982). "History of Air Pollution Legislation in the United States." *Journal of the Air Pollution Control Association* 32, no. 1, pp. 44–61, doi:10. 1080/00022470.1982.10465369, http://dx.doi.org/10.1080/00022470.1982.10465369.

<sup>&</sup>lt;sup>2</sup>Boston Air Pollution Control Commission, http://www.cityofboston.gov/environment/airpollution/, Main points in typical municipal definition of air pollution.

<sup>&</sup>lt;sup>3</sup>Philadelphia Air Pollution Control Commission, History of Air Pollution Control in Philadelphia, http://www.phila.gov/health/pdfs/History\_012013.pdf.

<sup>&</sup>lt;sup>4</sup>S. C Arthur. (1982). Emeritus Professor, the University of North Carolina. "History of Air Pollution Legislation in the United States." *Journal of the Air Pollution Control Association* 32, no. 1, http://www.tandfonline.com/doi/pdf/10.1080/00022470.1982.10465369.

Ringelmann number.<sup>5</sup> These monitoring charts are shown in Chapter 6.2. In an effort to be a good neighbor, some industries would even post the chart on the walls surrounding their factories for all to see that their smoke was lighter, or more gray, than smoke from neighboring factories.

By 1910, the City of Boston Air Pollution Control Commission had adopted the Ringelmann Smoke Chart as a relatively quantitative test. Their trained smoke readers could observe smoke density and determine which boilers were over the limit of a Ringelmann 1 smoke density (approximately 20% opacity) during boiler soot blowing for a few minutes an hour. Boston and many other air quality programs still have this general standard for visible emission levels in their regulations today.

The New York City<sup>6</sup> and Boston<sup>7</sup> definitions of "air pollution" were very similar to many others.

#### **New York City:**

# Emissions of air contaminants to the outdoor atmosphere of such quantity, characteristic, or duration which are injurious to human, plant, or animal life or to property, or which unreasonably interfere with the comfortable enjoyment of life or property.

## City of Boston:

ATMOSPHERIC POLLUTION means the presence in the ambient air space of one or more air contaminants in such concentration and of such duration as to cause a nuisance; or be injurious to human or animal life, vegetation, or to property; or unreasonably interfere with the comfortable enjoyment of life and property or the conduct of business.

Cleaner equipment was becoming available, but replacing existing furnaces would be expensive. The Air Pollution Control Association was founded in 1907.8

<sup>&</sup>lt;sup>5</sup>US Department of the Interior, Bureau of Mines, Ringelmann Smoke Chart, Information Circular 8333, 1977, (revision of IC 7718, 1955), https://www.cdc.gov/niosh/mining/UserFiles/works/pdfs/ic8333.pdf.

<sup>&</sup>lt;sup>6</sup>Notwithstanding the existence of specific air quality standards or emission limits, this prohibition applies, but is not limited to, any particulate, fume, gas, mist, odor, smoke, vapor, pollen, toxic, or deleterious emission, either alone or in combination with others. 6 NYCRR 211.1.

<sup>&</sup>lt;sup>7</sup>City of Boston, Regulations for the control of atmospheric pollution, Adopted December 17, 1976, General Laws of the Commonwealth of Massachusetts Section 31C, Chapter 111, http://www.cityofboston.gov/images\_documents/air\_pollution\_tcm3-13124.pdf.

<sup>&</sup>lt;sup>8</sup>S. C Arthur, Emeritus Professor, the University of North Carolina. (1982). "History of Air Pollution Legislation in the United States." *Journal of the Air Pollution Control Association* 32, no. 1, http://www.tandfonline.com/doi/pdf/10.1080/00022470.1982.10465369.

## 5.2 AIR POLLUTION PROGRAMS

In the second half of the 20th century, municipalities began to develop more effective measures and strategies for addressing the serious challenges that emission sources posed to society and ecosystems, and they established air pollution control agencies and departments.

After World War II, the population of Los Angeles grew rapidly and brought large numbers of automobiles into the air basin. Smog levels in the basin were notorious. In 1947, the County formed the Los Angeles Air Pollution Control District to study air quality problems and enforce measures that could clean up the air.<sup>9</sup>

Other city governments had health departments with broad general powers to prevent nuisances. Within a year of the Donora, Pennsylvania smog episode (1948), the Philadelphia City Council passed an ordinance to establish an Air Pollution Control Department (APCD) in the Bureau of Health. The Department was to define specific powers and duties, provide for administration, enforce, determine, and collect appropriate penalties for non-compliance. The Department began its work in 1949 under the direction of an APC Board. The APCD became a section in the city's Environmental Health Services in 1954, and that year passed ordinances prohibiting open burning and limiting smoke emissions. The smoke control efforts of the new Philadelphia APCD resulted in significant PM and SO<sub>2</sub> reductions—between 1956 and 1963 sulfur dioxide concentrations decreased almost 50%, and particulate declined by 25%.

The Baltimore, Maryland, City Health Department, like many others, had general powers to control nuisances. The subsequent Maryland policy was a good example of many air programs around the country. As described by the Maryland DEP on the Department website, "Maryland's work to stop air pollution fell to the Bureau of Sanitary Engineering in the Department of Health, which sometime between its creation in 1910 and 1951 acquired a vague supervisory interest in aerial pollution." Maryland uses the terms "air resources" and "reasonable degree of purity" in its regulations.

Exactly how clean did the ambient air need to be to protect human health and welfare? General nuisance is a difficult thing to measure or regulate. And these nuisances were not confined to something tangible, like a river, or geographical area, and could not be easily collected and tested for contamination. The effects of most of the great air pollution incidents were hard to link to specific chemical doses or emitters.

<sup>&</sup>lt;sup>9</sup>South Coast Air Quality Management District, History of Air Pollution Control in Southern California, http://www.aqmd.gov/home/library/public-information/publications/history-of-air-pollution-control The Southland's War on Smog: Fifty Years of Progress Toward Clean Air (through May 1997), http://www.aqmd.gov/home/library/public-information/publications/50-years-of-progress.

The requirement for "Generally applicable environmental standards for the protection of the general environment" appeared in the federal Atomic Energy Act of 1954. "Standards mean limits on radiation exposures or levels, or concentrations or quantities of radioactive material, in the general environment outside the boundaries of locations under the control of persons possessing or using radioactive material"—these could be standards for either air or water quality. Definitions of "ambient air" were being shared around the U.S. To quote from the Boston ordinance, ambient air was "the unconfined space occupied by the atmosphere above a geographical area." Under the Atomic Energy Act, models were developed to predict the dispersion plumes of radiation releases in the ambient environment and what concentrations would result downwind.

Researchers and governments were determining the source(s) of air contamination and developing control rules and emission inventories.

Out of the extraordinary air pollution episodes and the new threat from airborne radioactive materials came a series of federal efforts to research health and welfare effects and to design research programs and measures that could prevent harm to the public.

In 1955, the 84th U.S. Congress passed Public Law 159—Chapter 360, "the Air Pollution Control Act" (P.L. 159-360, or "APCA") in order "to provide research and technical assistance relating to air pollution control." With this two-page law, the United States formally recognized "the dangers to the public health and welfare, injury to agricultural crops and livestock, damage to and deterioration of property, and hazards to air and ground transportation, from air pollution." It declared that Congressional policy was to "preserve and protect the primary responsibility and rights of the States and local governments . . . in controlling air pollution."

The state, county, and municipal governments had vested the authority to control nuisance and air pollution in their health departments, and the new Federal law followed suit. It authorized the Surgeon General of the Public Health Service (PHS) in the Department of Health Education and Welfare (HEW) to be the lead federal office on air pollution research and support. Any of the municipal and state departments or bureaus officially charged with addressing air pollution were defined as "air pollution control agencies" ("APC agencies").

This first, federal APCA was enacted as a new section of the Federal Water Pollution Control Act, which in 1948 had already authorized the U.S. government to assist in preventing pollution.<sup>13</sup> In that law, the U.S.

<sup>&</sup>lt;sup>10</sup>PL 84-159 Chapter 360, 69 Stat 322, July 15, 1955, 42 USC 1857, et seq, http://uscode.house.gov/statviewer.htm?volume=69&page=322.

<sup>&</sup>lt;sup>11</sup>APCA §2(b)(3), PHS duties.

<sup>12</sup>APCA §6.

<sup>&</sup>lt;sup>13</sup>1948. It evolved into the Clean Water Act 33 USC §1251.

government established its legal standing, under the federal interstate commerce authority, to control pollution in interstate waterways. It supported state and local government work preventing water pollution and coordinated cleanup programs for the many governments sharing the burden of individual, contaminated water basins.

The air pollution mandate for HEW and the PHS was similar: to provide federal support for researching, funding, and providing services to the state and local governments "in the formulation and execution of their air pollution prevention and abatement research programs." PHS, in cooperation with the state and local governments, institutions, and industries, would conduct and support "technical research to devise and develop methods of preventing and abating air pollution," prepare reports, and disseminate information. If requested by an APC agency, the Surgeon General could survey or study specific air pollution problems. It also included a section to prevent "foreign endangerment." If U.S. smoke affected Canada, the law was clear that the federal government was the organization that should address the issue.

Public Health experts around the world continued to see dirty air affecting their cities. The U.K. passed Clean Air Acts in 1956 and 1968. <sup>15</sup> In California. the South Coast and Bay Area Air Quality Management Districts were charged with improving and protecting the Los Angeles and San Francisco air quality. In the West, where the cities were smaller in population and more spread out, coal smoke did not present the largest, most significant source of air contaminants. Instead, it was industrial growth based on the World War II effort, new oil extraction and refining, and all the new residents who were driving cars. California researchers and air pollution agency staff had already been finding that automotive emissions were as much a contributor to dirty air as smoke, if not more. The persistent "smog" conditions led 16 California to set up a Motor Vehicle Pollution Control Board in 1960, which evolved into the California Air Resources Board in 1968. It set requirements to capture evaporative VOC emissions in 1961, and car exhaust limits for CO and HC in 1966.<sup>17</sup> Along that same track, in 1960, the U.S. Congress directed the Surgeon General to conduct a two-year study on substances discharged from motor vehicles to determine what amounts of discharges were safe for human health and to recommend what was needed to protect public health. 18

<sup>14</sup>APCA §3 and §4.

<sup>&</sup>lt;sup>15</sup>United Kingdom, Clean Air Act, Chapter 52 4 and Eliz2, http://www.legislation.gov.uk/ukpga/Eliz2/4-5/52/contents and Clean Air Act of 1968, Chapter 62, http://www.legislation.gov.uk/ukpga/1968/62/contents. Current Act is Clean Act Air 1993, Chapter 11, http://www.legislation.gov.uk/ukpga/1993/11/introduction.

<sup>&</sup>lt;sup>16</sup>California Air Resources Board, Key Events in the History of Air Quality in California, https://www.arb.ca.gov/html/brochure/history.htm.

<sup>&</sup>lt;sup>17</sup>California Air Resource Board, Brief History of the ARB, The Father of Air Pollution Control, https://www.arb.ca.gov/knowzone/history.htm.

<sup>&</sup>lt;sup>18</sup>1960 PL 86-493, 74 Stat 162, http://uscode.house.gov/statutes/pl/86/492.pdf.

Some of the early Air Pollution (AP) publications<sup>19</sup> were:

- a. U.S. Bureau of Mines: A study on Sulfur Dioxide (SO<sub>2</sub>) Chemistry and Removal from Waste Gases (1958).
- b. ASTM: Standards on Methods of Atmospheric Sampling and Analysis (1959)
- c. Air Pollution Control Association: Proceedings of the fifty-second annual meeting (1959)
- d. U.S. HEW: Atmospheric lead contamination meeting (1960)
- e. U.S. HEW: Atmospheric Emissions from Fuel Oil Combustion An Inventory Guide (1962)
- f. PHS: Aldehydes in Photochemical Smogs (1962)
- g. PHS: Air Pollution Measurements of the National Air Sampling Network Analyses of Suspended Particulates 1957–1961 (1962)
- h. PHS: Air Pollution in the National Capital Area (PHS 955, 1962)
- i. PHS: Hydrocarbon Air Quality Criteria AP-64 (1964)
- j. PHS: Compilation of Selected Air Pollution Emission Control Regulations and Ordinances; Prepared by Abatement and Control Development Programs (1968)

# 5.3 FEDERAL ACTION FOR AIR QUALITY IN THE UNITED STATES

Eight years after the APCA, in 1963, the 88th U.S. Congress passed a law named "the Clean Air Act." (PL 88-206). Congress "found" that air pollution was growing, it was "brought about by urbanization, industrial development, and the increasing use of motor vehicles, [and] has resulted in *mounting* [emphasis added] dangers to the public health and welfare." This U.S. law had a national purpose: "(1) to protect and enhance the quality of the Nation's air resources so as to promote the public health and welfare and the productive capacity of its population."

The Act authorized the Secretary of HEW to collect and disseminate research information, cooperate with all Federal departments and agencies, make research and program grants and contracts, and provide training and fellowships. Specifically, this research was looking for "basic data on chemical, physical, and biological effects of varying air quality" prevention and control, and "effective and practical processes, methods, and prototype devices for the prevention or control of air pollution." The Secretary "shall

<sup>&</sup>lt;sup>19</sup> Available at the USEPA National Service Center for Environmental Publications (NSCEP). Website, https://www.epa.gov/nscep.

<sup>&</sup>lt;sup>20</sup>US Congress, The Clean Air Act, 42 USC 1857, PL 88-206 (CAA1963), December 17, 1963, https://www.gpo.gov/fdsys/pkg/STATUTE-77/pdf/STATUTE-77-Pg392.pdf.

conduct research on the harmful effects" on health and welfare by known "air pollution agents" and when a particular "agent" was found to be harmful, "publish criteria . . . indicating the kind and extent of such effects of such air pollution agent in the air in varying quantities." If any air pollution agent was determined to be causing harm, PHS should compile and publish criteria reflecting latest scientific knowledge useful in indicting the kind and extent of effects, and better ways to remove sulfur from fuels. <sup>21</sup>

The Act mandated that the Secretary of HEW had the specific duty of encouraging cooperation in state, regional, and municipal air pollution prevention and control activities<sup>22</sup> and, "so far as practicable" to encourage uniform State and local laws. Other duties were to establish a coordinated national research and development program and accelerate research, including the investigation and surveys requested by state and local air agencies. If air pollution in an area endangered health or welfare, the Secretary could call a conference and request data and reports from the polluters to abate the pollution, charging \$100 per day after 30 days if there was no response.

This strategy followed the lead of the federal program for cleaning up the waterways. It held states responsible for reducing pollution releases from their industries and other sources in order to protect clean air and water. The Federal Water Pollution Control Administration in the Department of Commerce was responsible for setting water quality standards in the waters of the United States, which often defined the border between two states and served interstate commerce. Its authority, based on the constitutional principle that the federal government regulated commerce, was much more straightforward than the health-based authority for protecting the air. The interstate commerce principle had allowed federal authorities to require the development of river basin plans that would achieve health and welfare standards. The same commercial principle had allowed Congress to enact the Federal Insecticide and Rodenticide Act in the early 20th century, which had authorized the U.S. Secretary of Agriculture to ban pest control chemicals. The pesticide DDT was banned under this law in 1986 before its use led to wholesale and imminent collapse of entire ecosystems.

The commercial legal precedent led to the "Motor Vehicle Air Pollution Control Act" in 1965, <sup>23</sup> which gave the U.S. Surgeon General power to "prescribe . . . standards, applicable to emissions of…new motor vehicles"

<sup>&</sup>lt;sup>21</sup>CAA1963 §3 a) R&D for prevention and control b) publish, support and train in support of this research.

<sup>&</sup>lt;sup>22</sup>42 USC 7402. This included the legal authority for two or more states to set up joint pollution control program. No states ever formed a "compact" under this provision, preferring not to relinquish authority.

<sup>&</sup>lt;sup>23</sup>PL 89-272, Oct 19, 1965, https://www.gpo.gov/fdsys/pkg/STATUTE-79/pdf/STATUTE-79-Pg992-2.pdf. http://www.epw.senate.gov/envlaws/cleanair.pdf as amended through PL 108-201 2/24/04; full text, 465 pages.

causing "air pollution which endanger the health or welfare of any person." This type of pollution source was in every location and state, was manufactured in just a few factories, and was sold in nation-wide markets. Because the U.S. government authority to regulate interstate commerce was already well established, the law was clearly within federal authority. The approach would abate pollution at its source by requiring manufacturers to design and build cleaner engines. Congress directed the Secretary of HEW to set emission standards based on the proven ability of systems or devices to reduce automobile emissions. Cars manufactured in 1973 would have to be clean enough to meet these standards.<sup>24</sup> The 1965 law also provided for federal research on controls, ways to monitor fuel combustion emissions including vehicles, and fuel cleaning processes. It set up a Federal Technical Committee to support the continued efforts of the automotive and fuel industry to find pollution control devices and lower emission fuels.

Two years later, Congress began a stronger program to define acceptable ambient air quality concentrations and monitor and protect the air the U.S. public was breathing. The 1967 Air Quality Act (AQA) recognized that air pollution was not limited to municipal boundaries. It set up formal Air Quality Control Regions (AQCRs), and tasked PHS with researching ambient concentrations and determining acceptable contamination concentrations. Documents defining these concentrations for *criteria pollutants*, based on "criteria" to protect health and welfare, were produced during the late 1960s for five key pollutants—PM, SO<sub>2</sub>, CO, NO<sub>2</sub>, and HC.

The AQA included and restructured the earlier clean air laws. It set the goal "to maintain that degree of purity of the air resources of the State which will protect the health, general welfare and property of the people of the State." Air pollution control programs and research became Title I, Air Pollution Prevention and Control; the motor vehicle and fuel standards were pulled into the Act as Title II. It further defined the federal role in assuring clean, healthy air and the State programs necessary to have it.

Expansion of the research priorities in AQA Sec 103 (e) gave more power to the Secretary of HEW to identify an air pollution problem, call a conference, and then to recommend reasonable, suitable measures to prevent air pollution. These conferences, like the water pollution control basin enforcement conferences before them, advanced the abatement agenda. It brought the parties creating pollution and those affected by pollution face to face with the agencies trying to prevent pollution. After more than a decade of research, the PHS started to issue criteria for ambient air standards. The

<sup>&</sup>lt;sup>24</sup>J.R. Fleming, and B.R. Knorr. History of the Clean Air Act a guide to clean air legislation past and present, American Meteorological Society webpages, Legislation, https://www.ametsoc.org/sloan/cleanair/.

Secretary would define the AQCRs and the criteria "requisite" for clean air quality and also provide technical and cost data for emission control.

States were required to adopt ambient air quality standards (AAQS) for criteria pollutants protecting health and welfare and to establish programs to implement, maintain, and enforce the standards with abatement programs. They also had the responsibility to adopt an enforceable program within six months. If standards and a State implementation plan (SIP) were not adopted, the Secretary of HEW could set the standard and create a federal implementation plan. When interstate air quality continued to be worse than the AAQS, despite state SIPs, the Secretary could seek federal enforcement against either the state or a regulated emission source to abate the pollution. For air pollution within a state border, PHS would assist the state in its plan or, at the Governor's request, could bring enforcement action against polluters.<sup>25</sup>

Not many states moved quickly on their plans to limit industry emissions. Few urban areas met the clean air standards on the three year schedule of the AQA.

1970 was a milestone year for the environment. With a national environmental movement underway, the Congress approved the National Environmental Policy Act of 1969 (NEPA) on January 1, 1970. It required federal environmental reviews for all projects funded by the Federal government and a new Council on Environmental Quality (CEQ) to oversee the process. The 1st Earth Day was celebrated on April 22, 1970. While the Earth Day Teach-ins went on, Congress was working on a better program to protect air quality in the United States.

In July 1970, President Richard Nixon proposed, and Congress approved, a Cabinet reorganization that created a single federal environmental agency in his Administration. The United States Environmental Protection Agency (EPA) was born. The EPA was the integration of many existing environmental protection programs, including the Department of the Interior's FWPCA and FIFRA programs; HEW's PHS air pollution authority and Bureaus of Solid Waste Management, Water Hygiene and Radiological Health; and the Department of Commerce river management program. The stage was set for the new EPA to administer and enforce new clean air provisions in the legislative bill being hammered out in the Congress. Five months later, on the last day of the year, the President signed the groundbreaking Clean Air Act, Public Law 91-604 (CAA, PL 91-604), into law. A summary of the United States clean air laws through 1977 is presented in Table 5.1.

<sup>&</sup>lt;sup>25</sup>The AQA included a Solid Waste Law.

<sup>&</sup>lt;sup>26</sup>US EPA CAA, Overview of the Clean Air Act and Air Pollution Control, https://www.epa.gov/clean-air-act-overview.

Date	Law	Short title	Description
July 14, 1955	P.L. 84-159 Chap 360; 42 USC 1857; 69 Stat 322	Air Pollution Control Act	Air Pollution Control Act New Section of the Federal Water Pollution Control Act.
June 8, 1960	74 Stat 16286-493; 73 Stat 646		Extension https://www.gpo.gov/fdsys/pkg /STATUTE-84/pdf/STATUTE-84-Pg2086.pdf
Dec. 17, 1963	P.L. 88–206, 77 Stat. 392; 77 Stat 646; 42 USC 1857-1857g	Clean Air Act (CAA)	A law to improve, strengthen, and accelerate programs for the prevention and abatement of air pollution. https://www.gpo.gov/fdsys/pkg/STATUTE-77/pdf/STATUTE-77-Pg392.pdf
Oct. 20, 1965	P.L. 89–272, 79 Stat. 992; 42 USC 85	Motor Vehicle Air Pollution Control Act	Air Pollution Prevention and Control
October 15, 1966	P.L. 89-675 80 Stat 954	CAA Amendments of 1966	More flexible grants for state programs https://www.gpo.gov/fdsys/pkg/STATUTE-80/pdf/STATUTE-80-Pg954.pdf
			(continued)

Table 5.1. Evolution of U.S. pollution control and the Clean Air Act – A chronology

Grable 5.1. Evolution of U.S. pollution control and the Clean Air Act – A chronology (continued)

Date	Law	Short title	Description
November 21, 1967	P.L. 90–148, 81 Stat. 485; Title II, 81 Stat 499	AQA of 1967 National Emission Standards Act	§2, Title I, §101(3) https://www.gpo.gov/fdsys/pkg /STATUTE-81/pdf/STATUTE-81-Pg485.pdf
July 9, 1970	84 Stat. 2086	Reorganization Plan No. 3 of 1970	Creates the Environmental Protection Agency from Department of the Interior, et al, the Federal Water Pollution Control Act https://www.gpo.gov/fdsys/pkg/STATUTE-84/pdf/STATUTE-84-Pg2086.pdf
July 10, 1970	P.L. 91-316, 84 Stat. 416; PL 91-605, 84 Stat. 1713	CAA Amendment	"to provide for a more effective program to improve the quality An Act to extend the Clean Air Act, as amended, and the Solid Waste Disposal Act, as amended, and transfer to US EPA
December 31, P.L. 91-604 1970 84 Stat 167	P.L. 91-604 84 Stat 1676	CAA of 1970	The Clean Air Act; https://www.gpo.gov/fdsys/pkg/STATUTE-84/pdf/STATUTE-84-Pg1676.pdf
August 7, 1977	PL 95-95, 91 Stat 685	CAA Amendments of 1977	https://www.gpo.gov/fdsys/pkg/STATUTE-91/pdf/ STATUTE-91-Pg685.pdf
1978	PL 95-620		Powerplant and Industrial Fuel Use Act; responded to the oil embargos.

#### 5.4 THE CLEAN AIR ACT (CAA) OF 1970<sup>27</sup>

The Clean Air Act<sup>28</sup> of 1970 (CAA) was an ambitious change in the series of national and state environmental laws and regulations developed after World War II.<sup>29</sup> It advanced the cause of clean air in the United States enormously. The 91st Congress worked with the existing elements of the CAA and agreed on ways to strengthen the U.S. federal government role. When air pollution was involved, the Congress elevated the authority to protect public health from the state to the national level. The Act made the federal government a more effective agent to "protect and enhance the quality of the Nation's air resources," clean enough to "promote the public health and welfare." For the first time, it made the national government responsible for setting air quality standards for the air the nation breathed. And it backed up this new, national priority with national standard setting, schedules, and enforcement.

Although the federal effort to reduce air pollution, even interstate air pollution, had not been very successful up to that point, the local air programs and previous federal air pollution laws had laid the foundation for a national air quality program. The 1970 CAA was able to build on the earlier programs to enhance the standard-setting, planning, public, implementation, and enforcement components into a comprehensive program. The 15 years of Congressional and PHS work had made clear the need for air contamination thresholds to protect health and welfare. It also continued the program of research and control of emissions from mobile emission sources, transportation fuels, and motor vehicles.

## 5.4.1 TITLE I: AIR QUALITY STANDARDS AND STATE IMPLEMENTATION PLANS

The basis of the law did not change. 30 "The Congress finds:"

- many U.S. Metropolitan areas and airsheds are interstate,
- increasing amount and complexity of air pollution "has resulted in mounting dangers to public health and welfare,"

<sup>&</sup>lt;sup>27</sup>Public Law 91-190, approved January 1, 1970, 83 Stat. 855.

<sup>&</sup>lt;sup>28</sup>US Congress, PL 91-604, 42 USC 85, https://www.law.cornell.edu/uscode/text/42/chapter-85/subchapter-I.

<sup>&</sup>lt;sup>29</sup>It preceded the landmark Clean Water Act, PL92-500, by 2 years.

<sup>&</sup>lt;sup>30</sup>CAA §101; 42 USC 85 §§ 7401 to 7515.

- air pollution prevention and control "at its source is the primary responsibility of States and local governments," and
- "Federal financial assistance and leadership is essential" for effective programs.

Its main "purposes," remained in place:

- 1. "to protect and enhance the quality of the Nation's air resources so as to promote the public health and welfare<sup>31</sup> and the productive capacity of its population;
- 2. to initiate and accelerate a national research and development program to achieve the prevention and control of air pollution;
- 3. to provide technical and financial assistance to State and local governments in their air pollution prevention and control programs; and
- 4. to encourage regional air pollution control programs."

The Cooperative Activities<sup>32</sup> and research and training programs<sup>33</sup> continued with the federal government conducting and coordinating "research, investigations, experiments, training, demonstrations, surveys, and studies" on air pollution:

- · "causes,
- effects,
- · extent,
- prevention, and
- control."

The new EPA<sup>34</sup> took on the air quality work previously assigned to the Secretary of HEW. EPA would "render technical services" and financial support; and would research and "survey specific problems of air pollution in cooperation with any air pollution control agency." It was authorized to "establish technical advisory committees" and would provide training, fellowships, and grants. The information from these investments would be made public as well as provide "basic data on chemical, physical, and biological effects of varying air quality and other information" on air pollution prevention and control.

<sup>&</sup>lt;sup>31</sup>adverse effects on welfare include injury to agricultural crops and livestock, damage to and the deterioration of property, and hazards to transportation.

<sup>32</sup>CAA §102.

<sup>&</sup>lt;sup>33</sup>CAA §Section 103.

<sup>&</sup>lt;sup>34</sup>Some States also chose the name "Environmental Protection Agency" for their own environmental agencies.

The CAA of 1970 added federal research on focused epidemiological studies of air pollution effects on mortality and morbidity, and it mandated that EPA itself would "conduct clinical and laboratory studies on the immunologic, biochemical, physiological, and the toxicological effects including carcinogenic, teratogenic, and mutagenic effects of air pollutants."

The existing research on fuel contaminants from the Motor Vehicle Act was included—controlling emissions, cleaner and new fuels, evaporative vapor control, and better combustion efficiency. The Act was amended to find improved, low-cost techniques for:

- a. "control of combustion byproducts of fuels,
- b. removal of potential air pollutants from fuels prior to combustion, [not just sulfur], control of emissions from the evaporation of fuels, improving the efficiency of fuel combustion so as to decrease atmospheric emissions, and producing synthetic or new fuels which, when used, result in decreased atmospheric emissions."

The new law enhanced the grants and support for State Air Pollution Control Agencies and Interstate Air Quality Agencies or Commissions.<sup>35</sup> Rather than relying on designating Air Quality Control Regions (air basins) and holding enforcement conferences to pursue air pollution abatement, in four new sections, the CAA mandated state programs to achieve clean air and federal programs for national air standards, program approvals, and enforcement. Each State was required to submit an implementation plan (SIP) for achieving and maintaining national air quality standards in each of its AQCRs. EPA had to evaluate the plans and, if deemed adequate to meet NAAQS over the long-term, approve them.<sup>36</sup> The air quality status of all U.S. AQCRs would be identified as in attainment with the standards, non-attainment, or unclassified, designations that are tracked today in the EPA *Green Book*.<sup>37</sup>

The new Section 108 required that the EPA Administrator define and issue *national* primary and secondary ambient air quality standards (NAAQS). He had to publish a list of air pollutants that harmed public health and welfare that were emitted from "numerous or diverse mobile or stationary sources." Air quality criteria would be issued within a year for each pollutant on the list. As before, the criteria documents

<sup>35</sup>CAA §104, 105, and 106.

<sup>&</sup>lt;sup>36</sup>CAA §107 Air Quality Control Regions.

<sup>&</sup>lt;sup>37</sup>US EPA, Nonattainment Areas for Criteria Pollutants (Green Book), https://www.epa.gov/green-book.

would "accurately reflect the latest scientific knowledge" on health and welfare effects and concentrations associated with them, as described in Chapter 4.<sup>38</sup>

The NAAQS, based on the Criteria Studies, were to be set at pollutant concentration levels with averaging times and a margin of safety that would protect public health. The secondary NAAQS would "protect the public welfare from any known or anticipated adverse effects." Standards for pollutants whose criteria research had been issued before the Act was passed had to be proposed as federal regulations within 30 days, and become final by April 30, 1971.<sup>39</sup>

Within nine months of NAAQS issuance, States were required to submit SIPs, their air programs to achieve, maintain, and enforce the primary and secondary standards. SIPs needed to attain NAAQS air concentrations as expeditiously as possible, not longer than three years for the primary standards. EPA would approve these state plans for attaining the standards within 4 months,<sup>40</sup> and extensions of 18 months were permissible. The main SIP components are outlined in Table 5.2.

EPA needed to promptly develop and issue a federal implementation plan if a state did not meet the timelines or develop a SIP that could meet the standards. However, States could show that primary NAAQS could not be attained in three years for lack of available technology to reduce

**Table 5.2.** CAA section 110: Requirements for state implementation plans (SIPs)

Demonstrate NAAQS attainment	Required program elements
Emission limits	Staff and financial resources committed
Emission data	Monitor, compile, and analyze data on ambient air quality
Timetables	Review and approve new sources subject to federal emission standards prior to construction
Enforcement powers	Periodic automobile tailpipe testing for compliance with federal emission standards

<sup>&</sup>lt;sup>38</sup>CAA §108 Air Quality Criteria and Control Techniques.

<sup>&</sup>lt;sup>39</sup>CAA §109. National Ambient Air Quality Standards. Imagine the 114th Congress, 2015-6, setting a schedule like this.

<sup>&</sup>lt;sup>40</sup>CAA §110 Implementation Plans (a) and (b).

pollution from key emission sources or vehicles. Those states would be allowed to implement interim measures and a two-year extension.

If all went according to plan, by January 1977, all U.S. residents would be breathing clean air that met the health-based, primary NAAQS. 41

#### 5.4.2 FEDERAL EMISSION SOURCE CONTROL

In the CAA, EPA was authorized to set emission standards for nationally important groups of sources. The "New Source Performance Standards" (NSPS)<sup>42</sup> program was the national breakthrough of the idea that new facilities should be built "as clean as possible." "New" sources were those that began construction or modification after the NSPS were proposed as regulations. The standards had to be based on research on control techniques for various important source categories. The available research and future studies based on industry data and information would determine how clean new equipment would have to be. The precedent for requiring each new source to be as clean as possible became a principle guiding many regulatory programs.

The CAA defined "standards of performance" for new stationary sources as that "which reflects the degree of emission limitation achievable through the application of the best system of emission reduction." The NSPS were set at levels "which (taking into account the cost of techniques or technologies for achieving such reduction) the Administrator determines has been adequately demonstrated for controlling emissions." A "stationary source" was defined as "any building, structure, facility, or installation which emits" an air pollutant, and this broad definition clarified that the NSPS program excluded mobile, vehicular emission sources that were already regulated separately at the manufacturer's production line.

As with the NAAQS, the EPA Administrator had to publish, and subsequently revise as needed, a list. The list needed to address categories of sources determined to "contribute significantly to air pollution which causes or contributes to the endangerment of public health or welfare." Four months after listing, the EPA was to propose emission standards for each new source category, provide for public comment, and then issue the standards in 3 months. Innovations in emission control systems could lead to revised emission standards, lowering the emission standards as technology improved over time. The States had to apply the emission rate standards from the national emission guidelines in their own permitting programs.

<sup>&</sup>lt;sup>41</sup>CAA §110 (c) to (f).

<sup>&</sup>lt;sup>42</sup>CAA §111.

It was declared "unlawful for any owner or operator of any new source to operate" in violation of the NSPS, and the EPA could enforce the NSPS and existing source standards directly. Nonetheless, if a State program included adequate procedures to implement and enforce the standards, EPA could delegate NSPS enforcement to the states, except for sources owned and operated by the U.S. government. In this way, States could still choose to run comprehensive air pollution control programs once they were approved as the delegated agent for carrying out the federal authority. The States were responsible for controlling existing sources in the NSPS list of source categories.

Another new program in these amendments required that EPA set national emission standards for hazardous air pollutants (NESHAPs). HAPs were contaminants that could increase mortality or serious irreversible illness but were not covered by an NAAQS. This program applied to specific types of new and existing sources emitting listed and regulated HAPs. NESHAPS regulations would be issued in a manner similar to the NSPS and could be enforced directly by the EPA. During the hearings on these proposed standards, the public could present the case that the emissions to be regulated did not meet the CAA definition of HAPs. NESHAPs applied 90 days after the regulations took effect, and an existing source could have a waiver of up to two years for installing controls. However, if there was no current control technology and operating the source was necessary for national security, the President could exempt that source for two years with two-year extension periods. The NESHAPs program could be delegated.

The CAA gave the SIPs strong federal support. EPA could identify violations of the SIPs and then issue a compliance orders or bring civil actions after a 30-day notice to the "person" (generally a source owner or operator) in violation. 44 If violations were found to be a systemic problem of the SIP, EPA would notify the state and the public, marking the start of a "period of federally assumed enforcement." EPA could determine violations of the federal NSPS and NESHAPS standards and enforce them immediately. It could also enforce the approved SIP requirements, after notifying the State. Those charged with EPA enforcement orders related to the SIPs were allowed to request a conference with the Administrator prior to civil actions, but EPA could issue injunctions.

The new enforcement powers extended to a new Section 114 that officially authorized EPA and the state agencies to gather the information

<sup>&</sup>lt;sup>43</sup>CAA §112.

<sup>44</sup>CAA §113.

needed to determine violations or develop air programs and standards. <sup>45</sup> Emission source owners and operators were required to:

- 1. keep records,
- 2. report,
- 3. install and use monitoring equipment or methods,
- 4. sample emissions, and
- 5. provide requested information.

In addition to information gathering authority, EPA had the right to access emission sources to inspect records and monitoring equipment and to sample emissions.

States and agencies were free to make additional emission standards and abatement requirements necessary to achieve clean air as long as they were not more lenient than a *promulgated* (adopted and approved) SIP, NSPS, or NESHAP. The EPA was instructed to consult with advisory committees and experts before publishing federal air pollutant criteria, lists, and standards. <sup>46</sup> The federal government itself was now subject to the CAA requirements, although the President could exempt a facility from a SIP as long as the reason was lack of funding appropriated for the source.

## 5.4.3 TITLE II: CONTROL OF AIR POLLUTION FROM MOTOR VEHICLES

Title II of the CAA, Part A, strengthened the 1965 Motor Vehicle and Fuel Standards Act and its 1967 amendments. HEW had set regulatory emission standards for pollutants<sup>47</sup> from classes of new motor vehicles or their engines that were judged to endanger health or welfare.<sup>48</sup>

The schedule for implementing the standards depended on how quickly, at a reasonable cost, the "requisite technology" could be developed. The CAA stated that CO and HC emission standards for model year 1975 and later had to be 90% lower than those in the 1965 law for light-duty vehicles (cars, small vans, and trucks), and NO<sub>2</sub> had to be 90% lower in model year 1976 cars than the tested average emission rate of uncontrolled model year 1971. The Congress knew that exhaust recirculation systems

<sup>&</sup>lt;sup>45</sup>CAA §114. When used by EPA, these information requests are usually in the form of "114 Letters."

<sup>&</sup>lt;sup>46</sup>CAA §116.

 $<sup>^{47}</sup>$ The term in  $\S 202$  of the 1965 Act had been "substances"; the CAA gave "pollutants" a legal meaning.

<sup>&</sup>lt;sup>48</sup>CAA §202 from (1965) Title II Motor Vehicles and Fuel Standards 7521-7554.

led to more complete combustion and lower emissions, but it also had been shown that small catalytic devices could reduce emissions significantly. It specifically left the choice of control system equipment up to the manufacturer.

By 1968, the new California Air Resources Board and its predecessors had already passed regulations containing maximum emission rates for automobiles and manufacturer registration and certification. <sup>49</sup> Because California had set strict car standards in order to meet its special smog challenges, the 1970 CAA allowed California to keep these stricter vehicle standards, but no other state could set additional emission limits. EPA would continue to set national emission source standards for mobile sources, but the stricter California standards could be adopted without change in other states.

Manufacturers were prohibited from making or importing and selling cars that did not meet the standards. All were prohibited from tampering with control devices prior to selling vehicles, and U.S. Courts could issue injunctions.<sup>50</sup> Penalties were raised to as much as \$10,000.<sup>51</sup> Testing to comply with a new certification program could be done by EPA or the state. Manufacturer records were required. Manufacturers had to warrantee that their equipment would meet emission standards for the vehicle's useful life.<sup>52</sup>

The CAA continued the 1967 requirement for fuel manufacturers and processors to register fuel additives and provide the federal government with the additive names, concentration range, and purpose. The new CAA gave EPA enhanced regulatory authority to control or prohibit additives that endangered health and welfare or impaired emission controls on the basis of science and economic data. Fines for violations could be up to \$10,000/day.<sup>53</sup> Grants were available for vehicle emission programs, and new inspection and maintenance (I&M) programs for vehicles in service had to be consistent with highway safety programs.<sup>54</sup>

The Act created an interagency Low-Emission Vehicle Certification Board. The one-year certifications were based on safety, reliability, serviceability and on noise, serviceability, and maintenance costs.

<sup>&</sup>lt;sup>49</sup>South Coast Air Quality Management District, Federal Air Quality Law, http://www.aqmd.gov/home/about/authority. CAA §208 was not revised – allowed only pre-1966 State standards. Only CA.

<sup>&</sup>lt;sup>50</sup>CAA §203 and §204.

<sup>&</sup>lt;sup>51</sup>CAA §205.

<sup>&</sup>lt;sup>52</sup>CAA §206, §207, with a Certification Board and approval process in Sec 212.

<sup>&</sup>lt;sup>53</sup>CAA §211. The EPA was also given authority to regulate under the Aviation Fuel Federal Aviation Act, Sec 601(d); Clean Aviation Fuels 75 USC 7581 – 7591.

<sup>&</sup>lt;sup>54</sup>CAA §210. 42 USC 7581 – 7591.

The Federal Government was to acquire low-emission vehicles for as much as 50% additional cost relative to standard vehicles.<sup>55</sup>

Under Title II Part B, EPA was required to study aircraft emissions and the feasibility of emission control. It would set standards for aircraft classes or engines that "endanger public health and welfare," and the Secretary of Transportation would prescribe compliance procedures in a manner consistent with DOT or FAA certification.<sup>56</sup>

#### 5.4.4 TITLE III – ENFORCEMENT AND ADMINISTRATION

The CAA gave the Administrator the power to bring suit in the U.S. District Court to immediately restrain persons and stop source(s) emissions "presenting an imminent and substantial endangerment to the health of persons" where state and local agencies "have not acted to abate" the pollution.<sup>57</sup>

A new principle in the U.S. legal system was built into this landmark law—*Citizen Suits*. *Any* person was permitted, had legal "standing," to bring a civil action in the U.S. District Courts against emission standard violators. A person could sue the EPA itself if it failed to carry out the Act. <sup>58</sup> Both the EPA and any person were given the right to intervene in a suit brought by another party. Administrative procedures for citizen suits, including notices, were spelled out. Federal contracts were prohibited for companies with CAA violation convictions, <sup>59</sup> and the President had to prepare an order for all federal departments to "effectuate" CAA policies and purpose in their contracts and grants. The Administrator was given the responsibility of reviewing the environmental impact of any action taken under the CAA, legislation, and regulations by the Federal departments and agencies and Federal construction projects. <sup>60</sup>

The Act also contained a Title IV – Noise Pollution and Abatement, which required EPA to create an Office of Noise Abatement and study the effects of noise on the public health and welfare, including urban noise levels and sonic booms. In conforming and technical revisions, the Public Health Service officers conducting research and training program

<sup>55</sup>CAA §212.

<sup>&</sup>lt;sup>56</sup>CAA §231 and §232.

<sup>&</sup>lt;sup>57</sup>New CAA §303-10 were inserted and the 1967 section designations were renumbered to 310-317. Under §305, the US Attorney General was to represent EPA; §307 administrative and judicial review procedures were spelled out; §308, patent right protections.

<sup>&</sup>lt;sup>58</sup>CAA §304 Citizen Suits!!!!

<sup>&</sup>lt;sup>59</sup>CAA §306 113(c)(1).

<sup>&</sup>lt;sup>60</sup>CAA §309.

support, who were transferred to the EPA when Nixon reorganized his cabinet, were allowed to remain in the PHS on assignment or become EPA civil servants.

And the generic "air pollution agents (or combinations of agents)" became "air pollutants."

# 5.5 STEPS TOWARD PROTECTING CLEAN AIR EVERYWHERE

EPA began recording acceptable air quality concentrations of PM and  $SO_2$  in AQCR after AQCR. EPA re-designations of state AQCRs in attainment for CO spread throughout the United States.

PM emissions decreased 50 percent between 1940 and 1980 (12.5 million Mg/yr), but SO<sub>2</sub> increased from stationary source fuel use from 15 million Mg to 22.1 million Mg (1970s). The element lead was added to the criteria pollutant list in 1976. The U.S. war in Vietnam came to a close. Two oil embargoes made the cheap price of U.S. gasoline skyrocket. Electric utility power stations were converted back to coal.

Nonetheless, many programs had not been able to reduce pollution concentrations sufficiently to meet the NAAQS, especially the standards for HC and photochemical oxidants.

#### 5.5.1 CAA AMENDMENTS OF 1977

The 1977 Clean Air Act Amendments made many general improvements to the Title I standards and SIP programs which continue today. In the years following the 1970 CAA, planners, regulators, and technical professionals had used different techniques and rarely met due dates. More research, studies, and programs beyond the 1970 CAA program were needed to support stationary source pollution abatement and achieve clean air throughout the nation.

The amendments mandated that the States take stock of progress by submitting a list of their AQCRs designating whether they had achieved the NAAQs. If areas met NAAQS, the status of the area was to be classified "attainment," if not, "non-attainment." Lacking sufficient information on air quality concentrations, an AQCR would be "unclassifiable." Many areas still had OC/oxidant concentrations above the NAAQS—"smog" was not yet defeated—and there were still some non-attainment areas for other criteria NAAQS around the country. Everything that could "cause or contribute to air pollutant concentrations exceeding primary NAAQS"

was in the cross-hairs. In Sec 108, "technology and costs of emission control" was better defined as the "cost of installation and operation, energy requirements, emission reduction benefits and environmental impact of the emission control technology." On the mobile source front, EPA was directed to prepare guidelines for transportation planning and vapor control from fuel transfer and storage, improved transit and carpool/bus lanes, and programs to control car idling, traffic flow, bicycling, parking, carpooling, conversion to cleaner fuels, and cold weather start-ups. 61

Because of the 1977 CAA Amendments, SIPs required periodic review, periodic emission inventories to determine if *reasonable further progress* (RFP) had been accomplished, more public participation, and ways to better control emissions of vehicles on the road. All emission sources, new or existing, had to be considered for emission reductions in non-attainment areas as the States pared down their emission inventories to attain the NAAQS. A source had to show that the "technological system of continuous emission reduction . . . will enable it to comply with standards of performance" (emission rate limits) and other CAA requirements before its Title I permit could be issued.

The "transportation control measures" included inspection and maintenance programs (I&M), fuel vapor emissions, and transit and anticongestion measures. Indirect source review was required: the evaluation of mobile sources and "*indirect sources*," the facilities that "attract" them, e.g., parking garages, large urban development projects.

The amendments specified that EPA was to prepare a more comprehensive list of NSPS source categories. Standards needed to be completed for listed categories on a five-year schedule. All categories needed numeric standards of performance. The standards had to reflect the degree of emission reduction achievable through the application of the best system of continuous emission reduction that had been demonstrated. "Best" was required to consider the cost of achieving such emission reduction and non-air quality health and environmental impact and energy requirements the Administrator determined had been adequately demonstrated. However, if a standard was infeasible or could not be measured or enforced, then design, work practices, or operating standards could be issued until a number could be set. Non-numeric control measures could similarly be issued for HAP emission sources, if "adequate to protect public health with an adequate margin of safety." No source could be required to install a particular emission reduction technology, and inherently low-emission processes, fuel cleaning, and innovative technologies were all acceptable means of meeting the standards.

<sup>61</sup>CAA1977 §103, PL 95-95.

The background documents for controlling these sources have a wealth of information developed from research and data collected from the industries via Section 114 letters.

Reflecting the oil embargo, energy supply disruptions of the 1970s, the Amendments said that if an order had been issued for a facility to convert to coal from petroleum or natural gas, the conversion project "shall not be deemed to be a modification" required to meet NSPS. The President was given the power to suspend air program requirements in national energy or economic emergencies. In the event of energy emergencies when jobs were lost and homes did not have heat, Governors could petition the President for SIP suspensions of up to four months if the suspension would alleviate the emergency and other means of response were inadequate.

The law increased the maximum penalty for violations from \$10,000 to \$25,000 per day. Compliance and consent orders could be used to extend the due dates for specific sources under new SIP rules, although a source requesting a delay in a non-attainment area had to show its impact was insignificant. International impacts were to be curtailed through the findings of an abatement conference.

The Amendments also included provisions for protecting visibility, a treasured air quality value of the American West. Sources that contributed to regional haze, caused by emission sources many miles upwind of the pristine areas in the West and in all the national parks, had to implement the best available retrofit technology (BART) to reduce emissions.

#### 5.5.2 PRECONSTRUCTION REVIEW TO ACHIEVE NAAOS

But the biggest change written into the 1977 CAA Amendments was a two-part federal New Source Review (NSR) program that regulated construction of new, large emission sources nation-wide. Major emission sources had to follow a uniform, federal, preconstruction review process to obtain their air permits. The permitting requirements were laid out in great detail for attainment areas and included drastic new emission control measures in non-attainment areas.

NSR was added to the CAA Title I: Programs and Activities, in two parts. Part C, the Prevention of Significant Deterioration (PSD), was designed to make sure that air quality in the areas that had achieved the NAAQS would not degrade and new emissions in these clean air areas would not cause problems downwind. Part D was a short, broad outline for how to obtain emission reductions for new major sources that could eventually lead to attainment of the NAAQS.

Under both parts of the new NSR, large individual stationary sources seeking approval for pre-construction permits were required to present information about their project and proposed emission control techniques that would result in emission rates being as clean as possible. This foundational part of both NSR programs was important to assure that emission rates from each new, major stationary source would decrease. New sources could not add to the poor air quality in non-attainment areas or degrade air quality in clean, attainment areas as economic development occurred and vehicle use increased. Emissions and control effectiveness were to be evaluated on an individual source level during permitting. In this way, advances in control measures would become official more quickly than the EPA national industrial research for NSPS could accomplish.

The Prevention of Significant Deterioration (PSD)<sup>62</sup> program in Part C, Sec 160 of the 1977 Amendments had its own clean air goals:

- 1. protect public health and welfare from adverse effects in water or soil caused by air pollution,
- 2. protect the pristine air quality of areas held in trust for the American public, <sup>63</sup>
- 3. define ways to allow economic growth and emission increases without exceeding NAAQS and
- 4. prevent interstate pollution.
- 5. evaluate consequences and consider "informed public comment" in making permit decisions.

The Congress spelled out many details for the PSD program in the law, and they are still applicable today. On a case by case basis, each preconstruction permit application for a *major* project in an attainment area needs to determine how low its emissions can be and how much these emissions will increase ambient pollutant concentrations. A new major source in an attainment area can emit only a mass of pollutants that would contribute no more than a small increment above baseline air quality concentrations. Public parks and wilderness areas over 2430 hectares (6,000 acres) are designated as pristine, Class I areas, with very small incremental concentration increases allowed. Most others are Class II, where more degradation, higher pollutant concentrations, can be accommodated. Particulate increments can not be more than 19 μg/m³ or SO₂ more than

<sup>&</sup>lt;sup>62</sup>CAA1977 §160 – 169.

<sup>&</sup>lt;sup>63</sup>Class I areas include all International Parks; memorial parks and wilderness areas > 5,000 acres (2025 hectares); and national parks > 2430 hectares.

 $20 \mu g/m^3$  (annual geometric mean). The full set of increments is spelled out in charts in the law that were carried into the NSR regulations.

To predict if a source can lower the air quality too much in an area, a source applying for a permit needs to apply a plume dispersion model to 1) predict the ground level concentration at the maximum impact location and 2) add this impact to the current air quality baseline. A year of continuous monitored data for the facility location is required to determine baseline air quality. In many cases, the nearest state monitoring site could provide this data.

PSD uses two methods of determining the "size" of a source and whether it is a "Major Emitting Facility." First, the 1977 Amendments contained a list of sources which are considered PSD "Major Emitting Facilities" (in attainment areas) if they have the potential to emit more than 100 tons per year (90.7 Mg) of any attainment pollutant. Based on the NSPS list started by the 1970 CAA, the list includes facilities in nationally important industries, businesses operating across the American markets that had significant emission sources. The PSD list in the regulations<sup>64</sup> included utility fossil fuel-fired steam-electric plants capable of generating approximately 73 MW; zinc, copper, and lead smelters; large municipal incinerators; iron and steel mills; and more. PSD construction review of all other types of large facilities and emission sources is based on "major" sources with a higher emission threshold. Emission capacity higher than 250 tons (227 Mg) of pollutants each year defines sources as "major" PSD sources.

No major emitting facility can be constructed in an area that attains the NAAQS without a permit based on its PSD review. Its emissions are not allowed to cause or contribute to air pollution over the PSD increments or NAAQS, and the facility is subject to the Best Available Control Technology (BACT). BACT is a facility specific "emission limitation based on the maximum degree of reduction of each pollutant . . . which the permitting authority, on a case-by-case basis, taking into account energy, environmental and economic impacts and other costs, determines is achievable." Available methods, systems, and techniques, including fuel cleaning or treatment or innovative fuel combustion techniques, need to be considered.

If the Federal Land Manager of nearby Class I areas finds that a facility would have adverse impacts on air quality-related values, no permit can be issued. The public also has to have the opportunity to comment on the proposed permit, the facility's impact, alternatives, and the control technology proposed. To protect the vistas in Western and other Class

<sup>6440</sup> CFR 50 and 51 list. 40 CFR 51.166, 52.21.

<sup>65</sup>CAA 1977 §169 (3).

I areas, facilities that could impair visibility have to install the Best Available Retrofit Technology (BART) to reduce visibility limiting emissions.<sup>66</sup>

To strengthen the non-attainment area programs, in three pages, Part D "Plan Requirements for Nonattainment Areas" sets new emission reduction requirements and metrics for how SIPs would show "reasonable further progress" toward attaining the NAAQS.<sup>67</sup> The Amendments allowed another 10 years to meet the primary NAAQS, with SIP revisions to include reasonably available control technology (RACT) for existing sources and comprehensive actual emission inventories.

Part D includes NSR requirements that allow new major sources in non-attainment areas to be built, even though additional emissions can only exacerbate poor air quality conditions. It specifies that the sum of total allowable emissions from existing sources large and small plus the new source must be less than emissions at the time of the application. Details on how to offset the new emissions were left to EPA's regulatory planners (Sec. 173). Non-attainment NSR requires new sources to meet emission rates that reflect the most stringent limitation achieved by sources in the same source category, the Lowest Achievable Emission Rate (LAER).

SIPs must make reasonable further progress, tallied every three years, to show that emissions are reduced as the plans intended.

Because the additional emissions of a new source will always increase concentrations, NSR includes no requirements to predict new source impacts for non-attainment pollutants. In addition, many non-attainment areas are not attainment for ozone, created by hydrocarbons and oxidants in photochemical reactions, and single source impact models do not exist to predict impact concentrations with any reasonable accuracy.

#### 5.5.3 VEHICLES AND MONITORING PROGRESS

Title II's Motor Vehicle and Fuel provisions were amended, setting Model Year 1980 light-duty vehicle CO emission rates to be 7 grams CO and 1.0 gram NO<sub>x</sub> per vehicle mile, ultimately achieving 90% vehicle emission reductions compared with 1970 models. CA waivers could be granted, control systems need 100,000 mile (160,000 km) warrantees, and tampering with the emission control devices was prohibited. EPA had to research fill-pipe, on-board HC controls, and vapor recovery systems and to regulate if

<sup>6640</sup> CFR 50 Appendix K, 52 Federal Register 29383 (Aug. 7, 1987) Class I designations.

<sup>&</sup>lt;sup>67</sup>CAA1977 §171-173, https://babel.hathitrust.org/cgi/pt?id=mdp.39015077940651;view=1 up;seq=17, U Mi Library document.

determined to be desirable. Standards for heavy duty vehicles were specified for the 1985 model year, and particle controls were considered.

Title III amendments added economic impact assessments and a National Air Monitoring System to provide more consistent, reliable, and representative evidence of whether air quality had met NAAQS concentrations across the United States. EPA was mandated to standardize air dispersion modeling tools and evaluate the impact of the Act on plant closures and reductions in employment. Staff threatened with layoff due to activities required by the Act were protected. Vapor recovery systems for fuel depots and fueling stations were required. The charges to EPA included a study of economic approaches to air pollution control and railroad emissions.

The amendments settled many of the other court suits and provided guidance for the emergency procedures that were initiated by the CAA. But, as abatement, monitoring, and control programs gained traction, many more issues came to light.

#### 5.5.4 CLEAN AIR ACT PROGRESS

The NAAQS–SIP programs defeated the age-old problem of smoke pollution and decreased air pollution in general, but the tools authorized in the Act were not able to achieve clean air throughout the United States. Other, more complicated air pollution challenges became apparent. In the period after the 1977 Amendments, the regulations implementing the law spawned many suits about the SIPs, NSPS, HAPs, and NSR programs as well as long-range emission impacts. Although the Act included provisions preventing sources from causing or contributing to interstate pollution, environmental welfare effects alerted the public and regulators to unresolved air pollution and damage beyond state SIP borders.

Much more information about the role of HC and other emissions in photochemical atmospheric reactions was developed throughout the 1980s. At the same time, impressive technological advances in monitors and instrumentation made it possible to see individual chemicals at tiny concentrations in the air as well as in groundwater, human tissue, and other biota.

SIP Regulations restricting the sulfur content of coal and oil had inspired cleaner fuels, which decreased emissions so much that the SO<sub>2</sub> concentrations almost everywhere had come down to NAAQS levels. But in the Northeastern United States, acid rain was turning lakes crystal clear—no biota—and acidic. Dead trees and other parts of forest ecosystems were showing signs of extreme stress.

Some of the members of the 95th Congress<sup>68</sup> who had hammered out the 1977 amendments were concerned that acid rain and agriculture impacts had been left out and proposed a bill that same year instructing the United States to organize an international conference. However, energy security concerns came first, and the effort to start reducing acid rain did not become law. An environmental research bill passed both Houses in the fall of 1982, but President Reagan vetoed it. Renewed efforts to proceed with research were offered in the House again each year, and later another Acid Rain Act. The EPA internally budgeted time and \$3 million in pilot grants to study how acid rain air programs could be set-up and organized a new office to evaluate market-based incentive programs rather than older approaches identified as "command and control."

With air and water quality improving, Americans' environmental concerns turned to waste and hazardous chemicals. By the late 1970s, the amount of waste produced in the United States had increased dramatically, and many specific, new, harmful chemicals, synthesized in the laboratories and factories of the maturing petrochemical industry, were showing up in food and waterways, groundwater, and human tissue. Emissions and releases of some of these chemicals had been a target of programs since the 1950s, but hazardous compounds were found to be leaking out of old dumpsites and migrating into the water and air. The Resource Conservation and Recovery Act (RCRA) was passed in 1984, establishing a manifest record system to track hazardous waste and its transport from the waste generator to final, safe disposal, "cradle to grave."

Hazardous chemicals that had been dumped by a chemical plant no longer operating were found in the groundwater under a housing development built on an old, filled-in canal, Love Canal, near Buffalo. The incidence of cancer and other diseases among the residents was extremely high compared with other known locations in the United States and found to be the result of contaminated waste and air exposures. This tragedy became part of the national culture and heritage of the U.S. No one wanted these materials in their backyards and the Congress passed the Comprehensive Environmental Response Compensation and Liability Act (CERCLA, "Superfund") to pay for the cleanup. In late 1984, the public was alarmed when plant in Bhopal, India released a deadly chemical cloud that killed more than 5,000 people. The Emergency Planning and Community Right to Know (EPCRA) law was passed in 1986, included a list of extremely hazardous substances (EHS), including many that could be released as air emissions.

<sup>&</sup>lt;sup>68</sup>Rep Jeffords of VT. Also concerned about Atmospheric Fallout in general.

<sup>&</sup>lt;sup>69</sup>The author assisted the Northeastern states (EPA Region 1) in developing and winning these Acid Rain grants.

#### 5.6 CAA AMENDMENTS OF 1990

The 101st Congress finally addressed all these issues, producing CAA Amendments (CAAA) that were signed into law in November 1990. These amendments improved several parts of and the effectiveness of the SIPs, and they added federally enforceable air permits in a new Title V. The CAAA mandated better programs to protect the environment from SO<sub>2</sub>, HAP releases, and other chemicals, including those destroying the ozone layer.

#### 5.6.1 1990 CAAA – IMPROVING TITLE I PROGRAMS

The Title I SIP, NSPS, and NESHAPS programs were expanded in the CAAA, based on the decade of previous regulation and lawsuits, and these enhancements continue to apply today. The attainment timeline still remains at three years or "as expeditiously as possible."

States in the Northeast had been fighting for more than a decade to have the EPA federal air programs recognize the role of NOx in photochemical reactions and appreciate the magnitude of the impact of interstate transport impacts that were preventing attainment of the ozone standard. The amendments included a specific prohibition against emissions from one state contributing significantly to or interfering with NAAQS maintenance or visibility in the other. The amendments allow the Administrator to establish air pollution *transport regions* and a Northeast commission to assess interstate pollution.

SIPs are required to maintain inventories of actual emissions, and the attainment timeline remains at three years or "as expeditiously as possible." Non-attainment areas are to be designated "severe," with a 25-ton major source threshold if ambient concentrations are above a threshold, or if worse, "extreme non-attainment" where a source is considered to be major if it emits only 10 tons of non-attainment pollutants per year. Offsetting emissions for new sources in non-attainment areas have to be 10% greater than the new emissions and they have to be local emission reductions. NO<sub>2</sub> emissions can be considered in predicting when the ozone NAAQS would be attained.

Tough non-attainment areas could rely on emission reductions, RFP, on a three-year interval to substitute for the deadline to achieve the ozone or other NAAQS. Control measures relying on economic incentives can be used. EPA was instructed to develop VOC Control Techniques Guidelines (CTGs),

<sup>&</sup>lt;sup>70</sup>PL 101-549, 11/15/1990, enrolled bill, https://www.congress.gov/bill/101st-congress/senate-bill/1630.

and the resulting reasonably available control measures (RACM) are mandatory as part of non-attainment SIP revisions. Boilers that emit more than 25 tons  $NO_2$ /year need low polluting fuel or advanced NOx control technology, and information on emission limits and the control technologies that achieved them has to be submitted to a national RACT/BACT/LAER clearinghouse.

The CAAA includes measures to reduce rush hour traffic, and Title II requires reformulated gasoline-powered, vehicle fleets. Light-duty truck emission standards are mandated. The new Title VII has more details on enforcement, Title VIII regulates activities on the Outer Continental Shelf, and Title IX enhances the research programs.

#### 5.6.2 CAAA - ACID DEPOSITION CONTROL

Although virtually all areas had achieved the SO<sub>2</sub> standards by 1990, sulfur compounds continued to wash out of the air and turn lakes and soils acidic. The Congress added Title IV, Acid Deposition Control, finding that:

- 1. "the presence of acidic compounds and their precursors in the atmosphere and in deposition from the atmosphere represents a threat to natural resources, ecosystems, materials, visibility, and public health;
- 2. the principal sources of the acidic compounds and their precursors in the atmosphere are emissions of sulfur and nitrogen oxides from the combustion of fossil fuels;
- 3. the problem of acid deposition is of national and international significance:
- 4. strategies and technologies for the control of precursors to acid deposition exist now that are economically feasible, and improved methods are expected to become increasingly available over the next decade:
- 5. current and future generations of Americans will be adversely affected by delaying measures to remedy the problem;
- reduction of total atmospheric loading of sulfur dioxide and nitrogen oxides will enhance protection of the public health and welfare and the environment; and
- 7. control measures to reduce precursor emissions from steam-electric generating units should be initiated without delay."

Title IV includes a schedule for reducing  $SO_2$  emissions by 9,700,000 Mg (10 million short tons) from the 1980 inventory, about 50%, and  $NO_2$ 

by 1,815,000 Mg (two million short tons). A baseline of 5.6 million tons SO<sub>2</sub> total from all other sources east of the Mississippi was also set. The 1985 to 1987 emissions from the electric utility units (steam generators) larger than 25 MW had been recorded in the EPA National Acid Precipitation Assessment Program (NAPAP) Emission Inventory. This baseline for emissions from each utility plant became the facility "cap," and initial Phase 1 *allowances* were provided to cover the baseline emissions. Emissions avoided by energy conservation methods and qualified renewable energy from biomass, solar, geothermal, or wind generation can be deducted from the actual emissions of a utility group. Diesel fuel producers also have to achieve SO<sub>2</sub> reductions and were given up to 35,000 emission allowances for their "affected" sources.

Coal plants received the largest baseline allowances, since coal had the highest level of fuel sulfur content, but they needed the most reduction to meet the SO<sub>2</sub> standards. As the reduction schedule progressed, a plant could install a "technological system of continuous emission reduction," fuel cleaning or traditional sulfur scrubbers. The required reductions were in the 70 percent range and a scrubber system can achieve at least a 90 percent SO<sub>2</sub> reduction. This means that a plant that installs a scrubber ends up with extra allowances. Because Title IV also provided that EPA build a tracking and allowance transfer data system, plants can choose to buy (or sell) allowances rather than install controls. This new, market-based, control system is called a "cap-and-trade" program.

Title IV penalties for excess emissions are \$2000 per ton, in addition to potential penalties from the violation of not meeting reduction targets.

#### 5.6.3 CAAA – TITLE V FEDERAL OPERATING PERMITS

As in the 1977 Amendments, expanded new source permitting requirements are an important feature of the CAAA, with new requirements for businesses and industry. The new Title V operating permit program requires that air agencies must issue consistent, federally enforceable, operating permits to all major sources. The permits need to have:

- Limitations and standards, enforceable by both the EPA and other air agencies
- A schedule of compliance
- A requirement to submit monitoring reports every 6 months
- · Conditions reflecting all requirements of the SIP.
- Monitoring, recordkeeping, and reporting requirements adequate to bring violations to Federal court.

A mass emission quantity of 100 tons per year (90.7 Mg) of any criteria pollutant defines an operating source as a "major". Other sources defined as "major" under the NSPS, NSR, or HAP rules are also required to have Title V Operating Permits. Compliance certification by the designated Responsible Official is needed at least every year, and the state and local programs have to be supported by source-paid fees. Each agency issuing Title V permits also has to have a Small Business technical and environmental compliance assistance program.

### 5.6.4 CAAA – HAPS, ACCIDENTAL RELEASES, AND THE OZONE HOLE

In the 1990 CAA Amendments, Congress has demanded much more from the Section 112 HAP program. Only about a dozen HAPs had been regulated under the NESHAPS program in the 20 years since the 1970 CAA, and the Amendments include a list of 189 hazardous air pollutants. EPA was directed to make a list of categories of HAP emitting sources and to set up a program for major source emission control standards that was much more like the NSPS program. Coke oven batteries are called out as a priority source needing standards. Major HAP sources are subject to the maximum available control technology (MACT) emission limits issued as regulations after EPA's determinations.71 The control measures to be considered would reduce the volume of HAPs through process changes and materials substitution, enclosures, capture and treatment, and design or work practice operational standards. The Amendments require smaller (lower emitting) "area sources" to implement MACT control measures, too, with high concern for reducing health risks in urban areas. Standards were required for 40 categories in 2 years, 25% more in 4 years, another 25% in 7 years, and all of them within 10 years. 72 EPA needed to "establish and maintain an air toxics clearinghouse and center to provide technical information and assistance to State and local agencies" Others could also pay for the EPA reports "on control technology, health and ecological risk assessment, risk analysis, ambient monitoring and modeling, and emissions measurement and monitoring."

The Amendments mandated that EPA establish HAP deposition assessment programs for the Great Lakes, Lake Champlain, the Chesapeake Bay, and coastal waters. EPA also had to determine the risk of mercury emissions from Electric Utility Steam Generating Units and set regulatory

<sup>&</sup>lt;sup>71</sup>10 tons/yr of any individual HAP or 26 tons/yr of a facility's total HAP emissions.

<sup>7240</sup> CFR 63.

standards, if needed. Emissions from publicly owned wastewater treatment plants and hydrogen sulfide needed to be studied, as well as radionuclide emissions not regulated by the Nuclear Regulatory Commission.

The new section of the law called "Prevention of Accidental Releases of EHS" requires *Risk Management Plans* (RMP) for sources that store or use EHS over threshold quantities "known to cause death, injury or serious adverse effects to human health." It sets up an independent Chemical Safety Board and created a Risk Assessment and Management Commission to investigate policy and chemical risk assessment and management across all federal agencies and programs. The role of the Commission is to determine if consistent procedures should be applied and to which programs. The Secretary of the Department of Labor is charged with developing a Chemical Process Safety Standard under OSHA.

The international Montreal Protocol to ban certain chlorinated and halogenated compounds (HCFC) was ratified by the United States in 1988<sup>73</sup> and incorporated into the CAA Amendments of 1990. As described in Chapter 4, the international community had found that holes in the stratospheric ozone layer were caused by these synthetic chemicals, and nations that signed the protocol had to ban production and phase out their use. Part B of the CAA Amendments set up the program to protect the ozone layer.<sup>74</sup> All listed ozone depleting substances (ODS) need to be recycled, and service companies are required to use special equipment to evacuate and capture refrigerant CFCs from air conditioners, refrigerators, and other cooling systems.

<sup>&</sup>lt;sup>73</sup>US Department of State – Montreal Protocol on Substances that deplete the Ozone Layer, http://www.state.gov/e/oes/eqt/chemicalpollution/83007.htm, (accessed November 13, 2016). <sup>74</sup>CAAA §150. 42 USC 7450 et seq.

# THE ATMOSPHERE — TRACKING AIR QUALITY

The atmosphere is a dynamic part of the global system and moves more quickly than any other physical attribute except the turning of the earth itself. Heat and momentum processes of the atmosphere move the air, water, and contaminants in several spatial scales and timeframes and disperse emissions downwind from their sources. Much of the energy in the earth system originates from radiation from the sun.

## 6.1 COMPOSITION AND ENERGY OF THE ATMOSPHERE

The atmosphere, the collection of gas-phase chemicals surrounding the earth, is a fluid blanket of air. The gas molecules in the atmosphere are held to the earth by gravity. Three, distinct, atmospheric layers between the surface and an elevation of 87 km contain nearly 100 percent of the mass of the air. The first two layers create a very thin layer of air around the earth, a dimension only 0.8 percent of the earth radius, and the third, low density layer reaches to 1.37<sup>1</sup> percent of the radius. Virtually all weather and water is contained within the two layers closest to the earth surface.

The lowest part of the atmosphere, the *troposphere*, has a depth of approximately 12 km in the mid-latitudes and is the home of terrestrial life, playing a large role in the chemistry and chemical cycles that support life. Commercial jet aircraft travel at or near the top of the troposphere, at 10 km. The next layer, the stratosphere, extends from the top of the

<sup>&</sup>lt;sup>1</sup>US National Atmospheric and Aeronautic Administration (NASA), Earth Fact Sheet, http://nssdc.gsfc.nasa.gov/planetary/factsheet/earthfact.html, (accessed November 14, 2016). Distance to the center of the earth is 6379 kilometers (3,964 mi) at the equator.

troposphere to 50 km and plays an important role in some geophysical cycles and capturing or blocking the energy and heat input from solar radiation, especially the higher energy, *ultraviolet* (UV) wavelengths. The mesosphere reaches to an elevation of approximately 87 km. Satellites orbit the earth at the top of the fourth region, the thermosphere, some 140 km above the surface. Chemical diffusion in the thermosphere and the fifth layer, the *exosphere*, depends largely on the mole weight characteristics and whether the gases have enough energy to escape gravity.

The mass of the atmosphere, the "weight" in the context of earth's gravity, is approximately  $5.27 \times 10^{15}$  Mg and exerts an average downward pressure of  $1{,}012 \times 10^6$  dyne/cm² (1 Pascal, Pa). Atmospheric pressure varies with the air density, based largely on water content and temperature. At the surface of the earth, the density of the air in the atmosphere averages approximately  $1.35 \text{ kg/m}^3$ . At an elevation of 2 km, the density declines to  $1 \text{ kg/m}^3$ , and at the top of the troposphere, the density is more than an order of magnitude lower than at the surface,  $0.1 \text{ kg/m}^3$ .

Mixing due to heat and density differences occurs throughout the troposphere and stratosphere. Although the oceans, fresh water, and land store most of the heat in the earth system, the atmosphere transfers energy more quickly. Water and two other atmospheric gases absorb most of the energy.  $O_3$  absorbs energy from the UV radiation of the sun, and  $CO_2$  collects *infrared radiation* as it is radiated outward from the sun-warmed ocean and ground. Because the air of the troposphere is heated from the surface of the earth, as the elevation in the troposphere increases, the temperature decreases, at a rate of approximately  $7^{\circ}C$  per 1,000 m. The average temperature of the atmosphere is approximately  $15^{\circ}C$  at the surface of the earth, and it decreases to an average temperature of  $-40^{\circ}C$  at the top of the troposphere.

The temperature differential between the sun-warmed equator and the polar regions, as well as the decreasing vertical temperatures, create air circulation patterns. When air is warmer, the additional energy moves gas molecules more quickly, forcefully, and farther apart. Because a given volume, or parcel, of warm air near the ground has fewer molecules, its

<sup>&</sup>lt;sup>2</sup>P. O'Gorman, instructor, 12.003: Introduction to Atmosphere, Ocean, and Climate Dynamics, Characteristics of the Atmosphere, MIT Open Courseware, http://www.mit.edu/~pog/12.003//pdf\_slides/Topic2.pdf, (accessed February 8, 2017). Supporting Textbook: J. Marshall, R.A. (2007). *Plumb, Atmosphere, Ocean, and Climate Dynamics: An Introductory Text.* Boston, MA: Elsevier Academic Press. ISBN: 9780125586917.

<sup>&</sup>lt;sup>3</sup>O. Hutzinger, ed. *The Handbook of Environmental Chemistry*, Vol 1 Part A, the Natural Environment and the Biogeochemical Cycles, The Atmosphere, M. Schidlowski, Max-Planck-Institut fur Chemie, pp.1-2, Springer-Verlag, 1980.

density is less than colder air, and it rises. The cooler air above may stop its upward motion, but eventually it can mix with the higher parcels and cool, transferring and rebalancing the energy.

The force of gravity is not strong enough to drag the air, a fluid, above a specific place at the speed of the earth spinning, approximately 1180 km/hour at latitudes 45 degrees north or south. But the global air circulation driven by the temperature difference between the equator and the polar regions and the earth rotation sets up a "jet stream" of air at the top of the troposphere in the mid-latitudes, which moves at a speed of about 440 km/hour from west to east.

Above the troposphere in a thin layer at the interface between space and the atmosphere a reaction driven by UV radiation from the sun, some of the most energetic and harmful rays of the sun, generates O<sub>3</sub>. The UV radiation provides enough energy to split O<sub>2</sub> molecules into single oxygen ions. With the additional energy, oxygen molecules with three atoms, O<sub>3</sub>, are created, forming a protective *ozone layer* at an elevation of 22 to 23 km in the stratosphere. This layer absorbs the intense UV energy and reduces the energy that strikes the surface of the earth. The high-energy content of the ozone layer increases the temperature profile of the top of the stratosphere to nearly 0°C. The same, high-energy O<sub>3</sub> molecule is not as benign if present at the earth surface. O<sub>3</sub> in the ambient air harms respiratory health when animals breathe it, and it can damage vegetation and other components of the environment.

In the beginning of the earth, approximately 4 billion (thousand million) years ago, the first atmosphere was created from magma and volcanic gas releases as the nascent solar system and its planets cooled.

Early, relatively stable chemical and material flux cycles on planet earth developed after the oceans formed and land emerged. Three billion years ago, one-celled lifeforms evolved, filled the oceans, and began new chemical and energy transfer cycles, including the release of gaseous oxygen.<sup>5</sup> For hundreds of millions of years, the oceans absorbed this byproduct oxygen of the new microorganisms and reabsorbed it when it had leaked into the new atmosphere. But, approximately 2.33 billion years ago, the concentration of free oxygen molecules (O<sub>2</sub>) became high enough to escape from the water and "contaminate" the thin layer of gas covering the planet. This "Great Oxygenation Event" reached a stable balance

<sup>&</sup>lt;sup>4</sup>P. O'Gorman. instructor, 12.003: Introduction to Atmosphere, Ocean, and Climate Dynamics, Characteristic of the Atmosphere, MIT Open Courseware, http://www.mit.edu/~pog/12.003//pdf\_slides/Topic2.pdf, (accessed February 8, 2017).

<sup>&</sup>lt;sup>5</sup>University of California, Berkley, Introduction to the cyano-bacteria, architects of earth's atmosphere, http://www.ucmp.berkeley.edu/bacteria/cyanointro.html, (accessed November 14, 2016). These ancient bacteria use sulfur transfer for energy, with oxygen as a waste.

Table 6.1. Concentration of constituents in the modern atmosphere

Chemical	Concentration (by volume)	Comment
Nitrogen (N <sub>2</sub> )	78.1%	
Oxygen (O <sub>2</sub> )	20.9%	
Water (H <sub>2</sub> O)	1–4%	
Argon (Ar)	0.9%	Noble gas
Carbon dioxide (CO <sub>2</sub> )	0.04%	400 ppmv
Neon (Ne)	18	Noble gas
Helium (He)	5	Noble gas
Methane (CH <sub>4</sub> )	1.7 ppmv	
Nitrous oxide (N <sub>2</sub> O)	0.3 ppmv	300 parts per billion by volume (ppbv)
Carbon monoxide (CO)	0.05–2.0 ppmv	
Ozone (O <sub>3</sub> )	0.040 ppmv	40 ppbv

between the concentration of oxygen in the ocean and air over the course of only 10 million years.<sup>6</sup>

Today, the chemical composition of the atmosphere is mostly nitrogen,  $N_2$ , with a significant amount of  $O_2$ , as presented in Chapter 1. Table 6.1 shows the concentrations of the main constituents.

The atmosphere contains small amounts of other noble gases, neon, helium, krypton, and xenon at 18, 5, 1.0, and 0.08 ppmv, respectively. These and other trace concentrations of anything else are generally so low as to be non-detectable without the most sensitive monitoring instruments. Anthropogenic emissions contribute to increasing  $\mathrm{CO}_2$  concentrations and to the locally, variable concentrations of the gases in the 1 to 100 ppmv concentration range.

As noted in Table 6.1, the troposphere contains from 1 to 4 percent water vapor, depending on the air temperature and the environmental presence of liquid water.<sup>7</sup> Water vapor is the most variable gas in the

<sup>&</sup>lt;sup>6</sup>G. Luo, S. Ono, et al. (2016). "Rapid Oxygenation of Earth's Atmosphere 2.33 Billion Years Ago." *Science Advances* 2, no. 5, p. e1600134, https://dspace.mit.edu/handle/1721.1/103006. 

<sup>7</sup>Pidwirny, M. (2006). "Atmospheric Composition." *Fundamentals of Physical Geography, 2nd Edition*, (Date Viewed. December 12, 2016), http://www.physicalgeography.net/fundamentals/7a.html.

atmosphere. When the air rises and cools to the temperature of water condensation, it condenses the gaseous water into tiny liquid droplets, forming visible clouds. Most clouds form in the troposphere.<sup>8</sup>

An air mass in the troposphere influenced by heat energy with minimal motion/momentum forces is defined as a *stable* atmosphere. Over the short period of a single night or a cloudy day without precipitation, the atmosphere is often stable because without solar input, no additional energy must be distributed or stored. As air heats up in the morning, air currents develop from forces such as sun warming and surface disturbances, making the air near the surface more turbulent. On a sunny day, the energy input typically creates turbulence and air current mixing in the afternoon as air near the ground warms and rises.

Natural and human events have modified the contaminants in the atmosphere for long periods of time over the last billion years, changing its capacity to store energy.

Geologists have discovered that periods lasting millions to hundreds of millions of years have been characterized by significant temperature variations when the concentration of  $CO_2$  in the atmosphere has changed. Some 300 million years ago, tectonic plate movements split continents on the crust of the earth and released large amounts of  $CO_2$  from within the core. Because  $CO_2$  retains more heat than either oxygen or nitrogen, it caused the atmosphere, land, and water to absorb more sun energy and warm the planet.  $CO_2$  again increased dramatically 100 million years ago. These periods correspond with the eras when large amounts of vegetation were buried in the earth, later to become fossil fuels.

Several meteor strike events have added PM emissions and energy to the atmosphere in the last half billion years. The one that occurred approximately 65 million years ago, whose crater is at Chixculub, Mexico, is estimated to have released as much as 10<sup>16</sup> kJ. It set vegetation on fire around the world and created tsunamis and high winds. The dust, mineral PM, and smoke plume of this extraterrestrial impact, and others, may have reached a height of more than 20 km, well into the stratosphere. This would contaminate the upper atmosphere for long periods, blocking the amount of sunlight that could reach the earth surface and lowering average temperatures.

<sup>&</sup>lt;sup>8</sup>NASA. NASA Facts, The Importance of Understanding Clouds, https://www.nasa.gov/pdf /135641main\_clouds\_trifold21.pdf, (accessed July 18, 2017).

<sup>&</sup>lt;sup>10</sup>T.A. Hansen, and C.F. Koch. Cretaceous Period Geochronology, Encyclopedia Britannica, http://britannica.com/science/Cretaceous-Period, (accessed January 12, 2017).

<sup>&</sup>lt;sup>11</sup>Australian Museum. The Mesozoic Extinction Event, https://australianmuseum.net.au/the-mesozoic-extinction-event, (accessed September 2016 and later).

Major volcanic eruptions have also sent PM, ash, sulfur, and other gases into the atmosphere. The eruption of Tambora in Indonesia in 1815 emitted approximately 140,000 Mg of PM as high as 33 km into the atmosphere, resulting in colder temperatures around the world for almost a decade.<sup>12</sup>

Relatively small quantities of anthropogenic synthetic emissions have also modified the atmosphere. After World War II, chemists created chlorinated synthetic compounds (CFCs) that were so stable that they could migrate to the stratosphere without breaking down. When these CFCs reached the elevation of the ozone layer, the ozone and energy were high enough to start chemical reactions. As this happened,  $O_3$  was depleted, leaving gaps, or "holes," that allowed excessive UV to reach the surface of the earth. The international community banned the chemicals, and with fewer emissions, natural atmospheric processes have been able to replace the missing ozone.

#### 6.2 AIR MOMENTUM, WATER, AND WEATHER

Mechanical processes of turbulence and momentum move the location of gases in the atmosphere, in three dimensions and at various speeds. Dynamic mixing and heat balancing processes operate on both the local scale, 0 to 100 km, and *mesoscale*, 100 to 1,000 km. <sup>13</sup> Most prominent in the troposphere, winds and general atmospheric circulation mechanically move the air with the particles, moisture, and emissions it holds.

The moving air in the troposphere must flow over surface irregularities, mostly less than 2 km, and it becomes turbulent as it is pushed upward. Air blowing over the highest elevation mountain peak, Mt. Everest at 9.1 km, is still in the troposphere. The friction of the moving air in the boundary layer between the atmosphere and the earth surface also affects the movement of the air to some degree.

The atmosphere cycles the water and other key chemicals from oceans, lakes, and land to the atmosphere and back again. Temperature and heat balance drive the water cycle. When air is warmer, the saturation vapor pressure increases exponentially and more water is absorbed into

<sup>&</sup>lt;sup>12</sup>C. Oppenheimer. (2003). "Climatic, Environmental and Human Consequences of the Largest Known Historic Eruption: Tambora Volcano (Indonesia) 1815." *Progress in Physical Geography* 27, pp. 230–59. doi:10.1191/0309133303pp379r. http://journals.sagepub.com/doi/abs/10.1191/0309133303pp379ra.

<sup>&</sup>lt;sup>13</sup>US National Center for Atmospheric Research (NCAR). Scales of Atmospheric Processes, Tutorial for the Community Earth System Model (CESM), http://www.cesm.ucar.edu/events/tutorials/2016/lecture2-neale.pdf, (accessed May 8, 2017).

the atmosphere.<sup>14</sup> Air saturated with water is heavier than dry air at the same temperature, and when it is cold enough to condense the moisture, the droplets can become heavy enough to be released to the surface as rain and snow.

The weather is a manifestation of how the heat and momentum energy contained in the atmosphere mixes to come closer to equilibrium. Water is the primary energy storage media on earth, and the atmosphere is an active participant in the water cycle. Surface weather, winds, clouds, and storms occur mostly in the troposphere, but occasionally, when the energy difference between masses of air is large enough, the circulation and storms can move warm air and water vapor from the surface up through the troposphere and into the stratosphere.

Because solar radiation is relatively constant near the equator, in the tropical regions between latitudes 23 degrees north and south, temperature does not vary much throughout the year. The warm air in these tropical climates has high humidity, and the heat energy provides for a good deal of vertical air diffusion and storms, supplemented in a few regions by mountains pushing air into higher, cooler elevations. Large, typical circulation patterns in the atmosphere move heat energy in the tropics and two other bands of latitude between the equator and the North and South polar regions. <sup>15</sup>

The temperate zones in the mid-latitudes experience more variable temperature and humidity over the course of 7 to 30 days than the regions near the equator or the poles. Humidity is relatively higher in the air masses that have just passed over oceans and large water bodies. When the air mass warms over the land, it can contain more water vapor even though the relative humidity becomes lower. When warmer air diffuses higher into the atmosphere, or is pushed up to 1–2 km elevations on the side of a mountain range, the gaseous water condenses and changes phase to liquid, in clouds and precipitation. Western slopes of mountain ranges are usually the beneficiary of this water, depleting it before the air flows down on the eastern side. Precipitation removes contaminants from the air into soil and water systems, leaving air quality cleaner.

For much of human history, weather predictions have been based on temperature and cloud formations—the visible evidence of water at different elevations. But for more than a century, scientists have been

<sup>&</sup>lt;sup>14</sup>P. O'Gorman, instructor, 12.003: Introduction to Atmosphere, Ocean, and Climate Dynamics, Characteristic of the Atmosphere, MIT Open Courseware, http://www.mit.edu/~pog/12.003//pdf\_slides/Topic2.pdf, (accessed February 8, 2017).

<sup>&</sup>lt;sup>15</sup>National Oceanic and Atmospheric Administration (NOAA). National Weather Service, Introduction to Global Weather, The Jet Stream, http://www.srh.noaa.gov/jetstream/global/jet.html, (accessed July 20, 2017).

studying the heat, motion energy, and water differences between air masses, and the data have made the weather predictions more accurate over longer periods.

The heat and humidity differences at the boundary between air masses create wind and precipitation when cold air moves to displace or mix with warm air and the dew point temperature decreases. Masses of air, *fronts*, have similar temperatures, humidity, and momentum and can move as a unit. Both warm and cold fronts can slide under a slower moving air mass, blending the energy and water content from the surface up. Large, and often violent storms, including hurricanes and northeasters, are created at the air mass interfaces where temperature differences (energy levels) at the boundary of a water-laden air mass are greatest.

Fronts can also get stuck for several days depending upon atmospheric pressure and whether enough energy is available to start the air moving again. It is not uncommon for high pressure areas, with their denser, heavier air, to remain in place for a few days. In the case of summertime high pressure fronts centered on Bermuda, in the Atlantic Ocean, the circulation within a front can feed humid air from near the tropics into humid weather patterns and precipitation 1500 km away.

Certain atmospheric conditions can create a "stagnating high" in London, New York, Beijing or anywhere. But valleys are particularly suited to stagnant air, "restricted atmospheric ventilation." Examples are the Los Angeles, California basin, which has nearly 1600 m high mountain ranges surrounding it, the Meuse Valley in Belgium or the valley in Pennsylvania where the town of Donora is located.

Inversions, layers of colder air trapped at the surface because it is denser than warmer air aloft, are the most troublesome, stable air conditions. Short, morning inversions can often be identified by a light haze near the ground when overnight heat radiation has lowered the surface air temperature below that of the air in the first 350 to 800 m of the atmosphere. But when fronts stall out for more than a day, the pollutant emissions remain in the ground-level layer and accumulate as emissions are added on the subsequent days. The mixing height during an air pollution episode in New York City in late November, 1966, was below 700 m for the period, with average wind speeds in the stagnant layer less than 5 m per second. Measured SO<sub>2</sub> concentrations peaked at 0.97 ppmv. The peak PM concentration in nearby Philadelphia, Pennsylvania, was 322 µg/m<sup>3</sup>. 16

<sup>&</sup>lt;sup>16</sup>J. Fensterstock, and R. Fankhauser. *Thanksgiving 1966 Air Pollution episode in the Eastern United States, AP-45*, US Department of Health, Education and Welfare, National Air Pollution Control Administration, Durham, NC, July 1968. Search for "AP45" at https://www.epa.gov/nscep.

On longer time and larger spatial scales, the typical weather temperatures and precipitation quantities make up the *climate*. Climate balances the heat energy on earth.

## 6.3 ECOSYSTEMS AND CHANGES IN THE ATMOSPHERE

The atmosphere and its weather play a large role in the water, carbon, and nitrogen cycles of the earth, cycles vital to the chemistry and development of terrestrial ecosystems. Along with  $O_2$  and sulfur, these materials provide the foundation for generating food, providing a carbon energy cycle, and building the cells that make up life on earth.

Life forms rely on chemical reactions for energy supply and growth, and at the surface of the earth, where solar radiation is available, sunlight provides the basic energy for life.

Green plants capture the radiation energy from the sun as an input for a process known as photosynthesis. Photosynthesis uses light energy and  ${\rm CO_2}$  to produce organic carbon and hydrogen molecules that create the lowest link of the food chain, carbohydrates. The process produces oxygen and water as its main byproducts.

The oxidation reaction is the most efficient, biological process for releasing energy from carbohydrates. Animals and plants depend on respiration, this oxidation process, to use the energy stored in their food chain. The ultimate byproducts of respiration are CO<sub>2</sub> and water, and terrestrial life emits these to the air. Nonetheless, life first evolved in anaerobic conditions, reducing sulfur compounds for energy.<sup>17</sup>

Biota have made ecosystems in every part of the earth by using both types of chemical reactions. In the world today, creatures living near the surface have access to free  $O_2$ , but life also thrives in anaerobic conditions in the deep oceans and other sealed-off places where microbes or chemical oxidation reactions, such as rusting, have depleted the atmospheric oxygen. As discussed in Section 3.3—Chapter 3, people use the same oxidation and reduction reactions in processes invented by humans that produce gaseous pollutant emissions, which increase the total amount of emissions.

Life on earth uses the troposphere, ocean, and land surface as habitat, and climate, temperature, and water availability provide boundaries for what is possible. Life evolves to fill every niche as ecosystems make full use of all energy and organic materials in each environment. Individual

<sup>&</sup>lt;sup>17</sup>The deep ocean ecosystems found around vents from the core of the earth depend on sulfur energy reactions, too.

animals and plants may be able to survive seasonal and short-term weather changes bringing food and water scarcity, but others may die in a period as short as a single year. Others may be able to adapt to climate and food changes, allowing ecologies to have mechanisms that can sustain populations through changes with timeframes of 10 to 20 years. Many species, such as humans, whales and oak trees, must evolve over periods of more than 1,000 years to achieve genetic modifications that allow their populations to adapt to major changes in the climate or oceans.

Enormous biological changes have occurred each time the atmosphere and climate have been disrupted. After the Great Oxygenation Event, terrestrial ecologies evolved, changed the energy and water profiles of various areas, and began to support the stability of local climates. Crustal debris and smoke from events like large meteor impacts create enough atmospheric change to dramatically change the climate for hundreds of thousands of years.

During the periods when the atmosphere contains more CO<sub>2</sub>, the climate changes, and the water, carbon, and energy cycle changes greatly disrupt habitats for generations of lifeforms for many millennia. Ecologies respond to the warming events, with vegetation using the additional carbon to grow rapidly, eventually decreasing the ambient CO<sub>2</sub>. Some populations disappear, while other creatures are more suited to the new environment and evolve and flourish.

For example, the Chixculub meteor strike emissions of smoke and dust stayed in the troposphere and stratosphere for as much as 1,000 to 3,000 years and created a drastically different climate in a short period of time. Food chains collapsed and there were massive ecosystem changes. It is estimated that 70 percent of species became extinct. But a new group of small, warm-blooded animals, early *mammal* species, were able to adapt and survive. <sup>18</sup> In the 65 million years of evolution that led to human mammals, some of the other branches of the family had time to move back into the oceans from the shore and evolve into whales and other cetaceans.

The power of evolution has also allowed ecologies, even those in the polar regions, to adapt within the "short," geologic 20-40,000 year cycles of the last several "ice ages," although many species, like wooly mammoths, have become extinct. These periods, four times longer than recorded human history, were accompanied by a drop in the level of the oceans, as the ice caps and sheets expanded in the colder temperatures and turned large amounts of the fresh water into ice.

<sup>&</sup>lt;sup>18</sup>Australian Museum. The Mesozoic Extinction Event, https://australianmuseum.net.au/the-mesozoic-extinction-event, (accessed September 2016).

And then came humans, who discovered ways to tame and use fire to clear land and whose travel and farming emitted dust. For tens of thousands of years, the processes and activities of human civilization mimicked natural processes and cycles in a small-scale way. In general, smoke and dust would be dispersed by the winds or washed away by precipitation. But as people settled together in towns, the stable night atmosphere and days without breezes could experience high local concentrations of PM due to the amount and proximity of smoke emission sources. High concentrations of odorous chemical emissions from husbandry, animal waste, and rotting piles of vegetation could be detected nearby as a nuisance before wind could disperse the offensive compounds over a longer distance.

Human observations produced a cultural understanding of general weather conditions for the annual cycles, the seasons, and, over a longer timeframe, the climate. The earliest people used rain and temperature history, often with sun position in the sky, to know when to plant crops and when to reap. But general climate knowledge was not sufficient to predict rain or drought and other weather disasters, and many early civilizations based their predictions on the stars or reading omens that they believed spoke for the gods.

Settlements and industries developed, many in river valleys. Forests were converted to cities and agricultural fields. Cars became commonplace in the 1950s, and higher smoke stacks sent some emissions kilometers downwind and over local hills. But occasionally, as discussed above, when stagnant weather conditions concentrated pollutant emissions, deadly air pollution episodes occurred.

# 6.4 MONITORING AIR QUALITY – HOW CLEAN IS IT HERE AND NOW?

Monitoring of the spatial and temporal distribution of air temperature, movement, and contaminant concentrations provides information about air quality conditions and how they are influenced by, or influence, the condition of the atmosphere.

Human senses can detect certain characteristics of the atmosphere, its changes, and pollution concentrations. Humans can sense the energy of moving air, air temperature, and its water level (moisture). Smoke particles can be seen and gaseous sulfur compounds and many others can be detected by the nose. Human sensory observations produced the oldest weather records and predictions—from sweating to shivering and in the record of traditional wisdom such as "Red sky in the morning, sailors take warning" or joint pain heralding the approach of low pressure and a storm.

Various instruments to monitor air pressure, wind speed, temperature, and rain were invented before the Industrial Revolution, and weather readings have produced data that provide an historic record. One of the most common measurement units for pressure in the world is the level to which mercury will rise in a tube, 760 mm at 0°C at sea level.

As more scientific tools were developed, scientists began to gather quantitative data about air and water. As with precipitation, stream flow, and water purity data, researchers can develop historic trend information and contours of spatial distribution of air quality with a robust empirical data set of records of weather and ambient concentrations. With these, the boundaries for future conditions become better understood.

Scientists and weather observers in many industrialized countries have been monitoring and keeping reasonably accurate temperature, pressure, and water weather records, with consistent worldwide data dating back to the 1880s. <sup>19</sup> Temperature and precipitation records more than a century long present a reasonable view of climate and the distribution of storms, extreme temperature, and precipitation at the monitored locations, especially in the industrialized nations.

Weather balloons carrying radiosonde monitors have been measuring temperature, relative humidity, and pressure twice a day in the U.S. since the 1930s at various heights in the atmosphere. As they rise, the decreasing pressure values represent one method of measuring "height" in the atmosphere. Data are transmitted back and the tracking systems can also determine the wind direction and speeds.<sup>20</sup>

However, all of the weather records cannot be lumped together to create an average global temperature—calculation methods must adjust for the uneven distribution of individual monitoring locations. Weather monitors have been carried in space satellites, and they have provided excellent worldwide coverage and data, except at the poles. But, this record is only three decades long, a period of time not long enough to cover variation in climate trends.

Scientists have studied and invented algorithms to make reasonably accurate measures of global average surface temperatures and can now monitor the variations from average, called *anomalies*.<sup>21</sup> The Goddard

<sup>&</sup>lt;sup>19</sup>J. Hansen, R. Ruedy, M. Sato, and K. Lo, GISTEMP Team. (2017). *GISS Surface Temperature Analysis (GISTEMP)*, NASA Goddard Institute for Space Studies, 2010, https://data.giss.nasa.gov/gistemp/news/20170315/, (accessed April 16, 2017).

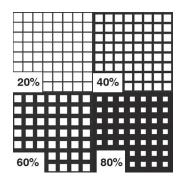
<sup>&</sup>lt;sup>20</sup>NOAA. National Weather Service, Weather Balloons, https://www.weather.gov/bmx/kidscorner\_weatherballoons, (accessed July 23, 2017).

<sup>&</sup>lt;sup>21</sup>NOAA. National Centers for Environmental Information (NCEI), Global Surface Temperature Anomalies, Background Information, https://www.ncdc.noaa.gov/monitoring-references/faq/anomalies.php, (accessed July 20, 2017).

Institute for Space Science (GISS, a laboratory in the National Aeronautics and Space Administration) has developed a method for determining average global temperature and has also built a model of the water and heat transfers and interaction of the oceans and the atmosphere.<sup>22</sup> It uses data from 6300 ship and buoy-based meteorological stations and adjusts for the lack of historical data in much of the world. GISS regularly evaluates climate warming or cooling trends and determines annual temperature variation from a baseline of the mid-20th century global average. GISS has developed the base year, average global temperature using 1951 to 1980 monitored data, which is 13.9°C (57°F). In 2016, the annual, average temperature was 14.8°C, and it was the hottest year on record.<sup>23</sup>

Significant advances in understanding climate and predicting global circulation patterns have been made by scientists all over the world since the International Panel on Climate Change (IPCC) was established in 1990, after the U.N. Earth Summit in Rio de Janeiro, Brazil. Researchers have developed complex, global-scale climate models, and monitoring data has confirmed major, large-scale ocean current and atmospheric circulation patterns. Because they store and move so much heat energy, the heat profiles of the major Pacific and Atlantic Ocean currents have been added to weather model inputs, improving seasonal predictions. U.S. weather reports often include the Pacific El Niño and El Niña currents as drivers for precipitation and temperature conditions.

Quantitative air quality monitoring, measuring the concentration of chemical contaminants in the air, began in a primitive fashion with smoke readers marking the blackness of a plume according to the Ringelmann Chart.<sup>24</sup> For over 100 years, smoke readers have been trained to distinguish emissions and certified for accuracy. Those with "calibrated eyeballs" also learn to distinguish water vapor plumes from smoke. Amateurs can distinguish smoke



**Illustration 2:** Ringlemann Smoke Chart

<sup>&</sup>lt;sup>22</sup>NASA. GISS Surface Temperature Analysis (GISTEMP), Frequently Asked Questions, Why can't we use raw data? Why does GISS show no data from before 1880? https://data.giss.nasa.gov/gistemp/faq/#q102, (accessed April 16, 2017).

<sup>&</sup>lt;sup>23</sup>NOAA. NCEI, Global Climate Report – Annual 2016, interactive webpage, http://ncdc.noaa.gov/sotc/global/201613, (accessed July 23, 2017).

<sup>&</sup>lt;sup>24</sup>US Department of the Interior, Bureau of Mines, Ringelmann Smoke Chart, Information Circular 8333, 1977, (revision of IC 7718, 1955), https://www.cdc.gov/niosh/mining/UserFiles/works/pdfs/ic8333.pdf.

and vapor plumes qualitatively by observing the plume at the tip of the stack. If the exhaust is steam, the opacity "vaporizes" into nothing downwind.

After the atomic bomb was deployed during World War II, monitors were used to record the distribution of radioactivity from aboveground bomb testing. Because radioactivity can be monitored real-time, with a single parameter, it was relatively easy to obtain ground level data.

In 1938, the Federal Works Administration established ambient "dust fall" and sulfur dioxide monitoring stations. <sup>25</sup> Conventional PM samplers filter a known amount of air through a nonreactive paper and are taken to a laboratory to be weighed, all according to precise, approved federal reference methods (FRM). Modern samplers differentiate PM<sub>10</sub> and PM<sub>2.5</sub>. Advances in technology have led to more automated, field sampling and analysis monitors that can take multiple, one-hour readings analyzed with a beta attenuation monitor (BEM) or a trademarked TEOM® monitor. Monitors can send data directly from remote monitoring locations. PM monitors have also been developed to take automatic readings of volcanic ashfall. <sup>26</sup>

The reproducible, quantitative detection and quantification of gases emitted from coal burning and other emission sources require more sophisticated monitoring. Pollutant concentrations in the ambient air were not very precise until sophisticated chemical monitoring and analysis devices that could detect chemicals in the ppmv range were developed in the early 1980s.<sup>27</sup> It is critical to select monitoring devices that can provide accurate results for the time period desired at ambient temperature and pressure conditions at a given monitoring location. Each sampling method will be affected by parameters specific to the pollutant, and each analysis method will have to minimize potential interferences.

Monitoring for  $SO_2$ ,  $NO_2$ , and CO can be done with electronic instruments with nearly continuous, real-time analyses. A UV fluorescence method is used in several  $SO_2$  monitors, and UV is part of the analysis method in several  $O_3$  monitors. "Long-path" or "open path" monitoring systems detect chemical wavelength signatures along a distance of 20 to 1000 m and have been approved in the U.S. for  $SO_2$  and ozone. CO samples are analyzed with infrared wavelength methods.<sup>28</sup>

<sup>&</sup>lt;sup>25</sup>California Air Resources Board, Key Events in the History of Air Quality in California, https://www.arb.ca.gov/html/brochure/history.htm#1938.

<sup>&</sup>lt;sup>26</sup>T. Shimano, T. Nishimura, et al. (2013). *Bull Volcanol* 75: 773, https://doi.org/10.1007/s00445-013-0773-7, December 2013, (accessed July 20, 2017).

<sup>&</sup>lt;sup>27</sup>US EPA. Air Monitoring Technology Information Center, AMTIC - Quality Assurance. https://www.epa.gov/amtic/amtic-quality-assurance.

<sup>&</sup>lt;sup>28</sup>US EPA. AMTIC, Air Monitoring Methods (EMC), https://www.epa.gov/amtic/amtic-air-monitoring-methods.

The EPA approves and publishes a *List of Designated Reference* and *Equivalent Methods*, for the criteria pollutants, linked to the Air Monitoring Methods—Criteria Pollutants webpage, https://www.epa.gov/amtic/air-monitoring-methods

In the 1930s, chemists began to develop analysis methods that could detect the set of complex, biological "organic" carbon compounds. Organic chemists devised methods for collecting samples of compounds being emitted from plants, and learned more about the fragrant emissions and other aromatic and non-detectible materials.<sup>29</sup>

Monitoring of emission concentrations is easiest to do at ground level, but hot, exhaust plumes rise in the atmosphere, moving vertically into the air and then spreading out in any direction from the equipment smoke stack, the emission point. The plume of emissions will be wide and deep enough to touch the ground at some distance downwind, but a monitor may not be far enough away or in the right direction from the stack to detect the pollutants. By the point in time when a plume of emissions from a specific source can be monitored on the ground, emissions of other sources in the vicinity may also be present, and the data are often a measure of combined impact.

Monitoring instruments today are capable of measuring parts per billion by volume gas concentrations. They operate effectively in ambient conditions around the globe and in high temperature gas streams and exhausts. Having extremely sensitive and accurate electronic monitors in the field eliminates the error introduced by sample containers and the time it takes to get an OC or other sample to a laboratory for analysis

Data from *continuous emission monitoring systems*, CEMS, installed in the exhaust stacks at EGUs and other major sources are available and considered in evaluating plume dispersion and impacts. *Continuous opacity monitors* (COM) are also on the market, and these measure opacity quantitatively. Based on maintenance needs and cost, COMs are a reasonable expenditure for large boiler installations.

Because the volume and mass of a gas sample vary with temperature and pressure, testing and analysis of air quality faces another challenge. The concentration of a pollutant in a liter of 80°C air will be representative of less mass (weight) of that pollutant than the same concentration in a cooler sample. Air quality data can only be compared accurately when the pressure and temperature of the gas samples are the same, or scientifically adjusted for their differences.

<sup>&</sup>lt;sup>29</sup>National Academy of Sciences. Arie Jan Haagen-Smit, 1900-1977, A Biographical Memoir, http://www.nasonline.org/publications/biographical-memoirs/memoir-pdfs/haagen-smit-arie.pdf, (accessed October 9 2016).

The air and weather monitoring station at the Mauna Loa Baseline Atmospheric Observatory in Hawaii was one of the first high-elevation monitoring locations when it was established by the Scripps Institution of Oceanography in 1956. At elevation of 3397 m above average sea level, it has monitored more than four decades of carbon cycle and other data, including CO<sub>2</sub>, ozone, wind speed, humidity, and wind direction. Mauna Loa also has LIDAR (Light Detection and Ranging) instruments, like some of the monitors on the EarthExplorer satellite and other locations, which use laser light pulses and reflections to monitor remote chemicals and air conditions. The satellite and other locations and air conditions.

Health and safety officials and researchers study air and water quality measurement records to determine trends and predictions for the relationship of contaminant concentrations to health and welfare. Sulfur dioxide monitoring was first done by placing materials, such as leaves, rubber tubing, or nylon stockings, at various locations and observing the rate and degree of degradation.<sup>32</sup>

Research published in the studies of the six criteria pollutants and the NSPS background documents includes the measurement methods that have generated the study data. The background documents for the NSPS also specify the monitoring methods for source emission rates, and results from compliance performance tests can therefore be compared across regions and types of sources. By setting regulatory monitoring methods, the accuracy of results and conditions and potentially interfering chemicals, like water, can be evaluated, and the methods themselves validated. The program for EPA method approval makes it possible to apply the standards fairly and reach for better methods.

Monitoring instruments on satellites provide an array of atmospheric and criteria pollutant information on a continuing and real-time basis. An example is the Measurement of Pollution in the Troposphere (MOPITT) monitors, orbiting the earth at 3,000 km on NASA's Terra satellites. They record CO and other concentrations in populated areas as well as the remote ones. In 2004, the drought in Alaska led to intense wildfires, consuming over 4.5 million hectares, and the data from that summer show that very high CO levels were present during that period, mostly produced

<sup>&</sup>lt;sup>30</sup>NOAA Earth System Research Laboratory (ESRL), Global Monitoring Division, Mauna Loa, Hawaii Observatory, https://www.esrl.noaa.gov/gmd/obop/mlo/, (accessed July 24, 2017.
<sup>31</sup>USGS. Light Detection and Ranging (LIDAR), https://lta.cr.usgs.gov/lidar\_digitalelevation, (accessed July 23, 2017).

<sup>&</sup>lt;sup>32</sup>National Academy of Sciences. Arie Jan Haagen-Smit, 1900-1977, A Biographical Memoir, http://www.nasonline.org/publications/biographical-memoirs/memoir-pdfs/haagen-smit-arie.pdf, (accessed October 9, 2016).

by the smoldering timber.<sup>33</sup> The DISCOVER-AQ studies in 2011 and 2013 found that satellite data could be processed and refined with air quality models to determine pollutant concentrations at ground level and other specific elevations.<sup>34</sup>

Since the 1970s, monitors have been gathering much more data on weather, ecologies, and chemicals from many more areas on earth. The set of air quality records is beginning to be large enough to understand past pollution trends, as is true of the weather data. Record gaps remain in some sparsely populated areas or those without government-funded programs. But the biggest unknown factor is how future emissions, forest cutting, city development, and agriculture will affect the natural energy, carbon, nitrogen, and water cycles. Trend analysis and predictions must use another approach—simulation models.

## 6.5 MODELING EMISSION DISPERSION, TRANSPORT, AND IMPACT

A set of modeling tools is necessary to relate emissions and ambient concentrations and evaluate whether current or future emission levels can preserve good air quality and a healthy natural balance. They help in predicting whether emissions from proposed sources will contribute to ambient concentrations above the NAAQS and whether required emission limits and reductions will be effective in achieving and maintaining clean air.

Weather models rely on physics principles to predict wind speed, wind direction, general air movement, and temperature. Standard weather models simulate short-term water, wind, and temperature conditions with relatively accurate predictions on a spatial scale of 100 to 1000 km and timeframes of several hours to a few days. Combined with surface and satellite monitoring data, especially radar detection, daily weather models and predictions have improved significantly over time.

Nonetheless, probability is still a major factor in determining the movement of each parcel and mass of air, heat transfer specifics, and when precipitation will occur. Predictions of the exact location of frontal boundaries and timing of weather cannot be completely accurate all the

<sup>&</sup>lt;sup>33</sup>Integrated Science Assessment. (ISA) for Carbon Monoxide (Final Report, Jan 2010), https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=218686&CFID=78776911&CFTO-KEN=81884369.

<sup>&</sup>lt;sup>34</sup>US EPA. *Tracking Pollution from the Skies (and Space!), Science Matters*, https://www.epa.gov/sciencematters/discover-aq.

time. For the same reason, models may never be able to produce precise, short-term predictions of complex atmospheric patterns like the jet stream.

Physics has been applied in relatively simple models of how emissions from a point, a vent or stack, will move. Standard dispersion models<sup>35</sup> calculate how the plume travels downwind under typical local, weather conditions. Most of these used in the U.S. assume that the exhaust plume and emissions spread out and disperse in the atmosphere according to Gaussian distribution factors. Hourly weather parameters and emission rates are prepared as inputs for the calculations. The model results are emission impact concentrations at locations up to 50 km away.

Weather data for dispersion models are based on the nearest weather station with an available data set. Five years of weather data is believed to be representative of all weather conditions. Parameters include surface and upper air hourly wind speed, temperature, and other factors related

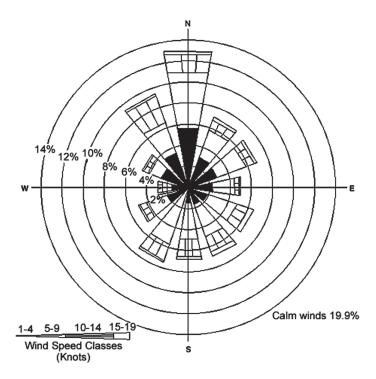


Illustration 3: Sample Wind Rose

<sup>&</sup>lt;sup>35</sup>US EPA OAQPS. Support Center for Regulatory Atmospheric Modeling (SCRAM), Air Quality Dispersion Modeling, https://www.epa.gov/scram/air-quality-dispersion-modeling, (accessed March 14, 2017).

to atmospheric stability.<sup>36</sup> In the simplest, screening form, a statistical set of hourly wind speed and direction and a grid of *receptors*, points where calculations will be done, is developed. The star-shaped graphic of the weather values is known as a *wind rose*.<sup>37</sup> Each weather condition in these data is applied in the model to determine the pollutant concentration of the plume as it arrives at the ground-level receptors. Most models have a switch that allows modelers to use stability parameters for either urban or rural areas.

A typical method for calculating mass hourly emission values is to use emission factors (EFs), as described in Chapter 3, to calculate emission inputs based on process activity levels, such as fuel use. This method is a consistent and generally accepted method for regulatory permitting determinations about whether a proposed new source will cause NAAQS violations. As presented in Chapter 3, EPA maintains an emissions modeling website and it has links to emission models and databases for smoke, biogenic, and other organic compound emissions and tools that prepare hourly emission inputs for dispersion modeling.<sup>38</sup>

Performance test data for a similar kind of source can be used in a model, or equipment manufacturer guarantees, and emission rates are converted to mass emissions per second. In air quality work, the *Universal Gas Law* is used to calculate mass emissions from the volumetric concentration data and the volume of gas being emitted.

$$pV = nRT$$

n = moles of the gas compound = (molar mass/g-mol)/molecular mass (atomic mass units)

p = pressure

V = Volume:  $m^3$  units

T = absolute temperature.

 $R = universal \ gas \ constant \ 0.08205 \ atm-m<sup>3</sup>/g-mole \ K; \ or \ liter-atm/Kmole<sup>39</sup>$ 

Because gas expands with higher temperature or lower pressure, all values must be calculated for a standard temperature and pressure.

<sup>&</sup>lt;sup>36</sup>US EPA OAQPS. SCRAM Observed Meteorological data, https://www.epa.gov/scram/air-modeling-observational-meteorological-data, (accessed March 14, 2017).

<sup>&</sup>lt;sup>37</sup>US EPA. Wind Rose PLOT, program and training files for download, 1993, https://www.epa.gov/scram/meteorological-processors-and-accessory-programs#windrose.

<sup>&</sup>lt;sup>38</sup>US EPA. Air Emissions Modeling, https://www.epa.gov/air-emissions-modeling, (accessed March 15, 2017).

<sup>&</sup>lt;sup>39</sup>Khan Academy. Ideal Gas Equation, https://www.khanacademy.org/science/chemistry/gases-and-kinetic-molecular-theory/ideal-gas-laws/v/ideal-gas-equation-pv-nrt, (accessed March, 12, 2017).

In most cases, air quality agencies use 15 or 20°C as the standard temperature. Measured from absolute zero on the Kelvin temperature scale, 20°C is 293.15°Kelvin. Because emissions in the environment are not constrained, the pressure can be assumed to be 1 atmosphere (101,325 Pascals).

Further mathematical algorithms simulate imperfect dispersion conditions. One provides for what happens to a plume lower than nearby hillside or mountain *terrain*, surface features, height, and contours. Another considers how a plume will be caught in surface air movement and building *downwash*, if the stack and associated plume height is not high enough to be at the level of relatively stable air flow.

EPA has worked together with the American Meteorological Society to enhance the regulatory dispersion models. The AERMOD Modeling System has software to process detailed input data, and is an upgrade from the Industrial Source Complex Short Terrain model (ISC3). Weather parameters reflect atmospheric turbulence as well as simple air flow. The associated input tool, AIRMAP, uses electronic U.S. Geological Survey data to lay out receptor grids in three dimensions more accurately and improves dispersion results for any area where the stack or plume height is lower than nearby terrain. <sup>40</sup> AERMOD is the first choice for emission source impact modeling in the US.

The CALPUFF model simulates emission dispersion in short puffs of exhaust and can represent dispersion reflecting more detailed wind directions and speeds. Originally designed for the California Air Resources Board, the model accommodates area source inputs, receptor grids as large as 100 to 1000 km, and chemical conversions. <sup>41</sup> CALPUFF does not ignore calm periods and inversions, and results have been shown to be comparable to those from ISC3. <sup>42</sup>

Point-source models like the AERMOD system calculate the starting height of the exhaust and emissions from the temperature at the tip of the stack, and simulate incremental plume movement. They have proven to be within 20 to 30 percent of empirical, monitored concentration results, and are approved by the EPA for use in air quality evaluations required by various regulations. It should be noted that the specific location of the

 <sup>&</sup>lt;sup>40</sup>US EPA. OAQPS, AERMOD Modeling System, https://www.epa.gov/scram/air-quality-dispersion-modeling-preferred-and-recommended-models#aermod, (accessed June 22, 2017).
 <sup>41</sup>J. Scire. (1990). Model Formulation and User's Guide for the CALPUFF Dispersion Model, California Air Resources Board, May 1990, https://www.arb.ca.gov/research/single-project.php?row\_id=50857.

<sup>&</sup>lt;sup>42</sup>US EPA. A Comparison of CALPUFF with ISC3, EPA-454/R-98-020, December 1998, https://www3.epa.gov/ttn/scram/7thconf/calpuff/calisc3.pdf.

highest or lowest impact is not exceptionally accurate. After all, a typical set of weather data is not what actually occurs.

Other screening model techniques developed by other agencies use different atmospheric parameters to determine a ventilation index, an estimate of whether good dispersion conditions exist. Used to evaluate the impacts of forest fires and agricultural burning, the Simple Approach Smoke Estimation Model was developed by the U.S. Forest Service and the state of Wyoming (SASEM). In the Willamette Valley in Oregon, a simple ventilation index calculation is done to determine if prescribed burning should be prohibited on a given day. The threshold values for bans include: whether the calculated ventilation index is less than 10, has there been one dry day for each 0.1 in rain, is humidity less than 30 percent and is surface wind over 15 mph (6.7 m/sec). The California ARB reviews several atmospheric parameters to determine if inversion conditions exist before allowing prescribed burning: height above sea level; atmosphere pressure; temperature difference at 3,000 feet (915 m); wind speed at 3000 feet; mixing layer wind direction, height; on-shore air flow.<sup>43</sup>

Other recommended models may be used to determine the impact of emissions that are not released from a point or to predict impacts of area or mobile sources. The National Forest Service has developed some of the fire risk and emission models such as TAPAS.

The CALINE3 and CAL3QHCR<sup>44</sup> models simulate dispersion of CO from roadways and highways and treat the mobile emissions as linear emission sources. Inputs are traffic signal timing, intersection layout, and the activity level of traffic at those intersections. The model can prepare results for daytime and nighttime, as well as 1-hour, 8-hour, and 24-hour averages.

Chemical analysis and reactions can be represented mathematically in models. *Receptor models* are based on detailed chemical analysis of PM, *fingerprinting*, to find correspondence between specific sources and receptors many kilometers downwind of the stack.

Air quality models have also been developed to predict exposures to criteria pollutant and HAP emissions. EPA and other agencies have investigated modeling systems to analyze health risk. The probabilistic model Air Pollutants Exposure Model (APEX) follows a single human receptor

<sup>&</sup>lt;sup>43</sup>US EPA, OAQPS. *Prescribed Burning Background Document and Technical Information Document for Prescribed Burning BestAvailable Control Measures*, p. 2-15, Research Triangle Park, EPA 450/2-92-003, 1992, https://nepis.epa.gov/Exe/ZyPDF.cgi?Dockey=00001X20.PDF, (accessed September 23, 2016).

<sup>&</sup>lt;sup>44</sup>US EPA. CALINE3 and CAL3QHC/CAL3QHCR Models, https://www.epa.gov/scram/air-quality-dispersion-modeling-preferred-and-recommended-models#cal3qhc.

through micro-environments to determine pollutant doses and risk.<sup>45</sup> The HAP Exposure Model (HAPEM) predicts concentrations affecting people in micro-environments, including indoors and in vehicles.<sup>46</sup>

Regional-scale models to predict or simulate O<sub>3</sub> air quality must include mechanisms for long-range transport and conversion of organic compounds (OC). The dynamic processes in photochemical atmospheric reactions generate a wide range of intermediate organic compounds with highly variable concentrations of oxidants present at different times and spatial distribution. In the 1980s, CARB developed CALGRID,<sup>47</sup> and EPA and the Northeastern state air agencies coordinated on a project, Regional Oxidant Modeling for North East Transport (ROMNET). By including NO<sub>x</sub> concentrations and simulations of chemical reactions, predictions of ozone concentrations became more accurate. The research convinced EPA that NO<sub>x</sub> reductions were necessary to improve control programs in areas that had not yet met the O<sub>3</sub> NAAQS. The U.S. Congress confirmed the new approach in the 1990 CAAA by designating NO<sub>2</sub> as an O<sub>3</sub> precursor and establishing an Ozone Transport Region covering areas from Washington, DC to Maine.

Visibility models predict long-distance visual impact of plumes containing SO<sub>2</sub> and PM, such as coal power plants. Proposed, major emission sources can obtain construction permits after meeting the requirements of the prevention of significant deterioration (PSD) permit programs. VISCREEN is the model approved to screen whether the new, stack emission plumes will be perceptible in national parks and other pristine public wilderness areas. If the model results show a possible impact, a further modeling study must then be done with the more detailed, more refined visibility model PLUVUE. Emission reductions are necessary if the simulation shows that the plume constituents will absorb visual wavelengths and be opaque to some degree, causing it to appear darker than the background, or if the plume will scatter light and appear brighter or lighter than the surroundings.<sup>48</sup>

<sup>&</sup>lt;sup>45</sup>US EPA. Human Exposure Modeling - Air Pollutant Exposure Model (APEX/TRIM. Expo inhalation), https://www.epa.gov/fera/human-exposure-modeling-air-pollutants-exposure-model, (accessed July 23, 2017).

<sup>&</sup>lt;sup>46</sup>US EPA. Human Exposure Modeling - HAP Exposure Model (HAPEM), https://www.epa.gov/fera/human-exposure-modeling-hazardous-air-pollutant-exposure-model-hapem.

<sup>&</sup>lt;sup>47</sup>R.J. Yamartino. CALGRID: A Mesoscale Photochemical Grid Model, User's Guide, Report No. AO49-1 September 1989, Volume 1, for CARB.J. Scire, SRC, Carmichael, G.R. University of Iowa, CALGRID: Report No. AO49-2, Volume 2, September 1989, for CARB, https://www.arb.ca.gov/research/apr/past/a6-215-74\_2.pdf.

<sup>&</sup>lt;sup>48</sup>US EPA. Workbook for Plume Visual Impact Screening and Analysis (Revised), EPA-454/92-023, https://www3.epa.gov/scram001/userg/screen/WB4PlumeVisualOCR .pdf, (accessed July 24, 2017).

Global-scale models are being developed to understand global warming, climate change, and how human activities and emissions contribute to the changes. The Fifth Assessment Report (FAR5) of the International Panel on Climate Change (IPCC) presents the latest information from many modeling studies predicting climate changes, including temperature, sea level rise, air and water circulation, and natural cycles. "The models used in climate research range from simple energy balance models to complex Earth System Models (ESMs) requiring state of the art high-performance computing. The choice of model depends directly on the scientific question being addressed." 49

The *Atmosphere-Ocean General Circulation Models* (AOGCM) simulate basic atmospheric, land surface, ocean and sea-ice conditions, <sup>50</sup> and the more complex *Earth System Models* (ESM) augment the results with aerosol, atmospheric chemistry, land carbon cycles, and an ocean biogenic component. Cloud, formation, boundary layer processes and radiation flux algorithms are rarely included with standard dispersion and environmental impact models, but must be included with this work to simulate the complex processes of the earth. A lot of work is being done to enable the models to share data and results and to improve them with monitored empirical data. The Physical Science basis webpages of the IPCC<sup>51</sup> provide concise responses to questions about the research and findings. For example, under FAQ 8.1, there is an explanation of the climate model reliability.<sup>52</sup>

Monitoring and modeling have revealed some of the secrets of the atmosphere, and they support efforts to protect air quality and healthy ecosystems.

<sup>&</sup>lt;sup>49</sup>UN International Panel on Climate Change (IPCC), Fifth Assessment Report, Chapter 9 Evaluation of Climate Models, page 746, http://www.ipcc.ch/pdf/assessment-report/ar5/wg1/WG1AR5\_Chapter09\_FINAL.pdf.

<sup>&</sup>lt;sup>51</sup>IPCC. Working Group 1, *Climate Change 2013: The Physical Science Basis*, report homepage, http://www.ipcc.ch/report/ar5/wg1/, (accessed July 25, 2017).

<sup>&</sup>lt;sup>52</sup>IPCC. FAQ 8.1, How Reliable are the Models Used to Make Projections of Climate Change?, http://ipcc.ch/publications\_and\_data/ar4/wg1/en/faq-8-1.html.

#### CHAPTER 7

## FUTURE CHALLENGES FOR AIR QUALITY

The first, national, air pollution control efforts have resulted in remarkable air quality improvement, yet challenges remain. Even though control measures for fuels, electric-generating stations, and mobile and stationary sources have led to better air quality in many local and mesoscale areas, work to reduce smoke and sulfur pollutant emissions continues in many parts of the world. Controlling emissions of just a few of the synthetic chemicals, such as polychlorinated biphenyls (PCBs), pesticides, and HAPs, has improved public health and produced a resurgence in many previously threatened ecosystems.

The progress has revealed unanticipated pollution problems. New information about health, long-range, and ecosystem impacts makes it clear that current ambient standards and pollution control programs are not fully sufficient to assure good air quality. Concerns about pollution from specific HAPs and chemicals are emerging from a better understanding of chemical reactions and conversions in the atmosphere and natural cycles. Ongoing studies are investigating long-range impacts and effects on ecosystems.

The approach and methods of the current U.S. and other air programs can be used by any nation to make further progress in reducing pollution. Because the emission limits for each large source permit in the U.S. are based on an evaluation of new control systems, proposed sources are being designed with lower emission rates. New engineering designs, electronic process control systems, and data systems equip emission sources to fine tune their operations for emission reductions. Any facility anywhere in the world can take advantage of advances in technology to decrease emissions and reduce pollution.

New monitoring and modeling tools will also help. Advances in the electronic, real-time, remote sensing of chemicals in the atmosphere, especially organic compounds, are a big step forward.

As time goes on, more sophisticated, health studies may result in several, lower, primary NAAQS. Agencies responsible for AQCRs that had been in attainment but exceed new standards will need to develop more pollutant reduction programs. For example, the annual PM<sub>2.5</sub> primary standard issued in 2013 is 20 percent lower than the original standard issued in 1997. The O<sub>3</sub> NAAQS was lowered to 0.070 ppmv in 2015, which means that even though the number of major smog episodes have dropped significantly, the list of areas exceeding standards is still long. Another example for continuing improvement is that almost all of the U.S. AQCRs met the original SO<sub>2</sub> NAAQS through fuel and power plant controls. However, to better correspond with recently identified, health-related impacts, the 3-hour primary standard was revised in 2010 to be slightly lower than the previous value. Because of advances in data collection and analysis tools, the EPA was able to base the new SO<sub>2</sub> NAAQS on a 3-year, statistical view of 1-hour readings rather than 3-hour averages.

Several long-range air pollution transport challenges have become better defined and are being worked on. Emissions have been tracked hundreds and even thousands of kilometers away from the sources, degrading air quality and affecting health and welfare far beyond the jurisdiction of the local agencies who regulate and permit them.

- In many cases, the PM<sub>2.5</sub> monitoring locations far downwind from recognized PM stationary sources are reading the concentration data that exceed the new PM<sub>2.5</sub> NAAQS. Agricultural area sources were not thought to be significant polluters, but PM reductions may be needed from them because the "haze" created by the secondary PM of the remote sources will not be easy to address.
- SO<sub>2</sub> emission reductions throughout the eastern part of the United States, required by a multi-state program, have allowed acidified lakes in the Eastern United States to recover. Nonetheless, many of the forests and ecosystems are still damaged and still show signs of distress. They may not be able to be restored to their original conditions, especially in light of the climate changes from global warming.
- The first global-scale problem related to a group of synthetic chemicals, CFCs, has been addressed by the international community.

<sup>&</sup>lt;sup>1</sup>US EPA. NAAQS Table, https://www.epa.gov/criteria-air-pollutants/naaqs-table.

<sup>&</sup>lt;sup>2</sup>US EPA. Particulate Matter (PM) Standards - Table of Historical PM NAAQS, https://www3.epa.gov/ttn/naaqs/standards/pm/s\_pm\_history.html.

<sup>&</sup>lt;sup>3</sup>US EPA. Ozone Pollution, 2015 National Ambient Air Quality Standards (NAAQS) for Ozone, https://www.epa.gov/ozone-pollution/2015-national-ambient-air-quality-standards-naaqs-ozone. <sup>4</sup>US EPA, Sulfur Dioxide (SO2) Primary Standards - Table of Historical SO2 NAAQS, https://www3.epa.gov/ttn/naaqs/standards/so2/s\_so2\_history.html.

- A precedent was set when all the nations of the world agreed to take coordinated action under the Montreal Protocol (1987),<sup>5</sup> which phased out and then banned the production, use, and emissions.
- Anthropogenic and biogenic OC emissions are difficult to track as
  they are transported and react—creating O<sub>3</sub> NAAQS violations in
  plumes of dirty air from areas of densely located stationary and
  mobile sources. It was necessary to set up the Ozone Transport
  Area (OTA) in the Northeastern United States to coordinate the
  air pollution control programs of the 10 states in adjacent O<sub>3</sub>
  nonattainment areas. The need to compromise affects the timing
  and implementation of control measures that will lead to O<sub>3</sub> levels
  meeting the standards.

HAPs and some of the tens of thousands of other synthetic chemicals can adversely affect health and welfare. Monitoring can identify metal pollutants, but it is much more difficult to monitor and confirm which toxic organic emissions or reaction products pose an exposure risk at a particular time and place. More work has been done to develop control measures for the known O<sub>3</sub> precursor OC emissions than to unravel the complexity of organic compound photochemistry in the atmosphere. More research is needed to understand airborne organic chemistry and achieve air quality concentrations that meet the NAAQS and protect public health.

The UN Earth Summit in Rio de Janeiro, Brazil, in 1990 raised concern about the global environment and how humans were affecting the climate, the seas, and the ecosystems. At the Rio Summit, the challenges of acid rain, rainforest preservation, and the effects of the CFC ban were hot issues, but the new issue of possible global warming was also debated, and the International Panel on Climate Change (IPCC) was established.

So much CO<sub>2</sub> has been emitted from fossil fuel burning that concentrations around the world have increased significantly in the past century, and scientists have learned that the higher concentrations are warming the earth.

By 1992, nations were starting to collect and share annual inventories of CO<sub>2</sub> and other GHG emissions that trap heat in the atmosphere. Scientists are developing reasonably accurate models of atmospheric fluxes, ocean currents, other heat transfer systems, and heat storage on earth. In 2017, hundreds of scientists and others researching global warming and the impact of climate change were still working on the Fifth Assessment Report (FAR). More is being learned about the forces causing the

<sup>&</sup>lt;sup>5</sup>Protocols are international legal agreements. The Montreal Protocol on Substances that Deplete the Ozone Layer, http://ozone.unep.org/en/treaties-and-decisions/montreal-protocol-substances-deplete-ozone-layer.

earth to warm and the role of fossil fuel CO<sub>2</sub> emissions in this potentially devastating change.

Although the impact of GHG emissions on global warming and climate is not yet fully understood, the international community has accepted the goal of keeping global temperature increases under 2°C. Information needed to achieve this goal is a complete list of the GHG chemicals, their biogenic and anthropogenic sources, and the emission quantities, locations, and timescales. Over the next few decades, researchers will have temperature data from an expanded network of monitors to validate climate and ecosystem models and measure success or failure. The models and more complete inventories will help engineers, economists, and politicians determine what control measures will be effective and possible.

Engineers, scientists, health professionals, lawyers, planners, politicians, and the public will all be needed to find solutions for the persistent challenge of protecting clean air.

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Sarah J. Simon, PE, has provided environmental protection services for government, industry, and consultancies for more than 40 years. Graduating as a civil engineer, she worked in construction and then as an engineer for water and air programs of the US EPA Boston Office. She participated in the national, award-winning team that established state acid rain programs and went on to direct the monitoring, database, and modeling staff of the Massachusetts Department of Environmental Protection air program. Over the past two decades, she managed environmental projects in a Fortune 200 company, consulting firms, and an energy services company generating green power. Simon has presented technical papers on the impact and compliance needs of energy projects, in particular, landfill biogas facilities. She led the Environmental Group of the Boston Section of the American Society of Civil Engineers and the Society of Women Engineers-Boston Section. She received the MIT Alumni Lobdell Award for organizing conferences and curating an exhibit of the alumnae group, AMITA.



